SUPERCRITICAL FLUID EXTRACTION

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TABLE OF CONTENTS

(i)

List of Figures

List of Tables

1. Introduction

1.1 Statement of the problem

The quantitation of trace amounts of organic compounds on environmental solids is comprised of three main steps; extraction of the compounds of interest, sample cleanup if required, and the actual analysis. The analysis step is relatively straightforward, and often automated. The first two steps, however, are very time consuming and laborious. The extraction step can take as long as 48 hours, requires large amounts of solvent(s), and is not usually very selective, a fact which necessitates the cleanup step. The cleanup step itself usually involves several procedures in order to further purify the extract. It would be advantageous to develop an extraction procedure which is rapid and which is selective enough so that further cleanup steps are not required.

1

1.2 Background of the project

The Ontario Ministry of the Environment solicited a proposal for research in supercritical fluid extraction in May, 1987. Dr. Peeter Kruus of the Chemistry Department of Carleton University was awarded a grant for a three year research program. The proposed schedule of activities was as follows:

87.09.01 - 88.02.29	Review of Literature
88.03.01 - 88.08.31	Assembling of Equipment
88.09.01 - 89.08.31	Fundamental Studies
89.09.01 - 90.05.31	Optimization of Equipment
90.06.01 - 90.08.31	Writing of Final Report

The grant was awarded beginning 88.03.01. This report is for the first six months of the project, and details theoretical and practical aspects of supercritical fluid extraction. A copy of the research proposal can be found in Appendix I.

1.3 Objectives

The objectives of the project are:

(i) To develop a rapid and reliable method for the extraction of trace organics from environmental solids using supercritical fluids in place of conventional solvents.

(ii) To develop methods for selective extraction of certain classes of compounds.

2. Description of a supercritical fluid

A fluid may be characterized by many physical quantities. The advantages of using a supercritical fluid for extractions, however, stem mainly from unusual variations of density near the critical point, and from transport properties that are intermediate between those of the corresponding liquid and gas. The properties of of a supercritical fluid of most interest are thus the density, viscosity, and diffusion coefficient. The dielectric constant of a solvent (including a supercritical fluid) can be used as a measure of its solvating power as well, although the influence of the variation of density is much larger than that of the dielectric constant.

2.1 Density

Strictly speaking, the conditions that define a supercritical fluid are those temperatures and pressures above the critical values T_c and p_c. This region is shown above and to the right of the dashed lines in figure 2.1 for carbon dioxide.

For simplicity, the temperature and pressure of a system are often stated in terms of their reduced counterparts:

$$T_r = T / T_c \qquad (2.1.1)$$

$$p_r = p / p_c \qquad (2.1.2)$$

where T_r and p_r are the reduced values of the absolute temperature, T, and the pressure, p.

The region generally of interest is $0.9 < T_r < 1.2$ and $0.9 < p_r < 3$. In the immediate vicinity of the critical point, the density of the fluid can be varied enormously by small changes in the temperature or pressure. An example of this is shown in figure 2.2, a plot of the reduced density versus reduced pressure at various reduced temperatures for CO_2. This phenomenon has utility because the solvation power of a solvent is related to its density, a point that will be discussed in more detail later. Examination of figure 2.2 shows that the density has increased from that of CO_2 gas to liquid-like values above p_c. It is important to note that the liquid phase as such does not exist at these conditions. Above

5

the critical point, there is only one phase.

2.2 Viscosity

The viscosity of gases below their critical points are essentially independent of pressure. Above the critical pressure, however, the viscosity increases with pressure. Figure 2.3 shows the variation of viscosity of CO_2 with respect to pressure at various temperatures. Below the critical pressure, the viscosity is approximately proportional to $T^{1/2}$. Above p_c, however, viscosity decreases with increasing temperature, an effect generally associated with liquids, not gases. The viscosity values shown in figure 2.3 are nevertheless lower than the viscosity of liquid CO_2. This is true of most supercritical fluids; their viscosities are almost an order of magnitude lower than those of liquids, or a few times higher than those of gases.

2.3 Diffusion coefficients

The diffusion coefficients for supercritical fluids are generally an order of magnitude higher than those of the liquids, but several orders of magnitude lower than those of gases. This allows extractions to be carried out faster in a supercritical fluid than in a liquid.

In general, the diffusion coefficient D_{AB} is inversely proportional to pressure below p_c but inversely proportional to the square root of pressure above p_c. The variation of D_{AB} with pressure is shown in figure 2.4 [2.1]. The data points are included in figure 2.4 to emphasize that no data was collected in the critical region, near 0.5 kg dm^{-3} (see figure 2.2). Other studies [2.2] indicate anomalous behaviour of the self-diffusion coefficient in this region.

2.4 Dielectric constant

According to the theory of Debye, the Clausius - Mosotti function $(\mathcal{E} - 1)V_m/(\mathcal{E} + 2)$, where $\mathcal{E}$ is the dielectric constant and V_m is the molar volume, should remain constant with increasing pressure, and should be given by [2.3]

$$(\mathcal{E} - 1)V_m/(\mathcal{E} + 2) = 4/3 \, \pi N(\alpha_o + \mu_o^2/(3kT)) \qquad (2.4.1)$$

where α_o is the mean molecular polarizability and μ_o the dipole moment. Experimentally, however, the Clausius - Mosotti function rises, then falls with increasing pressure, due to molecular interactions. The function is therefore expressed with 'dielectric virial coefficients' (in analogy with, but not to be confused with the coefficients of the virial equation of state);

$$(\mathcal{E} - 1)V_m/(\mathcal{E} + 2) = 4/3 \pi N(\alpha_o + \mu_o^2/(3kT)) + B/V_m + C/V_m^2$$

$$(2.4.2)$$

The experimental variation of the dielectric constant of CO_2 with density is shown in figure 2.5 [2.4].

3. Thermodynamic treatment of SCF systems

3.1 Equations of state

(a) Ideal

The equation of state relating temperature, pressure and volume of a pure substance may be expressed as

$$p = RT/V_m \qquad (3.1.1)$$

where R is the universal gas constant. This equation is the ideal gas law, and only approximates reality at low density.

(b) Van der Waals

The simplest equation of state which describes the critical region of fluids was proposed by Van der Waals [3.1]. This equation expresses the pressure as the sum of two terms, a repulsion pressure and an attraction pressure:

$$p = p_R + p_A \qquad (3.1.2)$$

The repulsive forces between the gas molecules tend to increase the pressure, thereby decreasing the effective volume. Mathematically, therefore, the V_m in equation 3.1.1 is replaced by (V_m - b), where b is a constant for a particular gas, which will in general be larger for larger molecules, since they will tend to reduce the effective volume by a larger amount than smaller molecules.

The attractive forces tend to reduce the pressure. The number of pair interactions is roughly proportional to the square of the concentration, or of the density. The reduction

10

in pressure is therefore a/V_m^2, where a is again characteristic of a particular gas. The gas law may now be altered from the ideal form (equation 3.1.1) to the Van der Waals form:

$$p = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2} \qquad (3.1.3)$$

When p is plotted versus V_m, a series of curves such as those in figure 3.1 are generated. Referring to figure 3.1, the curves are plotted at different reduced temperatures, T_r. T_c is the critical temperature, i.e. the temperature above which the liquid phase can not exist, no matter how high the pressure is. The inflection point on the curve at the critical point allows one to find the critical point in terms of the Van der Waals constants a and b. By realizing that the first and second derivatives of p with respect to V vanish at the critical point, the critical constants are found to be

$$p_c = a/27b^2 \qquad (3.1.4)$$

$$T_c = 8a/27Rb \qquad (3.1.5)$$

and $\qquad V_{c,m} = 3b \qquad (3.1.6)$

where $V_{c,m}$ is the critical molar volume.

These values suggest that the compression factor of any gas at the critical point, z_c, should be

$$z_c = p_c V_{c,m}/RT_c \qquad (3.1.7)$$

$$= 0.375$$

11

The experimental values of z_c are somewhat less than this value.

Equation 3.1.3 can be expressed in terms of the reduced variables p_r, T_r and V_r;

$$p_r = \frac{8T_r}{(3V_r - 1)} - \frac{3}{V_r^2} \qquad (3.1.8)$$

where $V_r = V_m/V_{c,m}$. This allows plots to be made relating p_r and V_r (at selected values of T_r) which are universal i.e. they are valid for any substance. Such a plot is shown in figure 3.2.

Note that to obtain figure 3.2, equation 3.1.8 was first expressed as a polynomial in V_r, and the roots were calculated numerically. (See Appendix II for the method of solving the Van der Waals equation.) The root corresponding to the gas phase was then used, and figure 3.2 presents the results above the critical temperature. The figure is plotted as $1/V_r$ versus p_r since the density is proportional to $1/V_r$ (see also figure 2.2).

(c) Peng-Robinson

Several variations of the Van der Waals equation have been proposed. For the purposes of predicting the solubility of solutes in supercritical fluids (covered in section 3.4), it is necessary to have an equation of state that describes

12

the supercritical region with some accuracy, and is easily extended to mixtures. Peng and Robinson [3.2] proposed an equation of the form

$$p = \frac{RT}{(V_m - b)} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} \qquad (3.1.9)$$

The main features of this equation are that the value of a (the intermolecular attraction constant) is temperature dependent, and that the repulsive pressure term has been replaced by a term which produces more realistic values of the critical compressibility factor, z_c. Furthermore, the value of a depends on the acentric factor ω (see below), a measure of the non-sphericity of the molecule.

Applying the Peng Robinson equation at the critical point yields

$$a(T_c) = 0.45724 \, R^2 T_c^2 / p_c \qquad (3.1.10)$$

$$b(T_c) = 0.07780 \, RT_c / p_c \qquad (3.1.11)$$

and $$z_c = 0.307 \qquad (3.1.12)$$

The temperature dependence of a is

$$a(T) = a(T_c)(\alpha(T_r, \omega) \qquad (3.1.13)$$

where $$\alpha = (1 + \kappa(1 - T_r^{.5}))^2 \qquad (3.1.14)$$

The constant   is a characteristic for each substance, and was found by Peng and Robinson to be a function of the acentric factor ω ;

$$\kappa = 0.37464 + 1.54226 \, \omega - 0.26992 \, \omega^2 \qquad (3.1.15)$$

13

The constant b is assumed to have no temperature dependence.

3.2 Effects of pressure and temperature on density

Whichever equation of state is used, the density of the solvent may be found from

$$\rho = MW/V_{c,m}V_r \qquad (3.2.1)$$

where MW is the molecular weight of the gas, and ρ is in $g\ L^{-1}$. Thus, for the Van der Waals equation,

$$\rho = MW/3bV_r \qquad (3.2.2)$$

and for the Peng-Robinson equation,

$$\rho = MW/3.946bV_r \qquad (3.2.3)$$

Figure 3.3 compares densities calculated from experiment with those from three equations of state for CO_2 at its critical temperature. The density is seen to increase with pressure along the isotherm, and the increase is especially large near the critical point. At higher temperatures, the density does not increase as quickly with pressure.

The density at any pressure decreases with increasing temperature. This fact has important implications in process scale applications of supercritical fluid extraction since a solute can be easily precipitated by increasing the temperature slightly. This method of recovering the solute can be more economic than decreasing, then increasing the pressure. The region of the critical point is of most interest because of the large variations of density with only small variations in pressure. At some specified temperature,

15

then, the density of the solvent can be tailored by varying the pressure. This has important implications for selective extraction of solutes.

It is apparent from figure 3.3 that the Peng-Robinson equation is more capable of predicting solvent densities above the critical point than the Van der Waals equation. Both are equally accurate at or below the critical pressure, however. The ideal gas law (equation 3.1.1) is accurate only at pressures well below the critical pressure.

3.3 Thermodynamics of binary systems

The discussion thus far has considered only a one component solvent. In order to extend the equation to multi-component solvents, it is necessary to replace the constants a and b with new values which depend on the values for each of the components, and on the composition of the system. The mixing rules are

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad (3.3.1)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \qquad (3.3.2)$$

where x_i is the mole fraction of component i, and a_{ij} and b_{ij} are interaction parameters. The interaction parameters for unlike components (i≠j) are related to the pure component parameters by

$$a_{ij} = (1-k_{ij}) (a_i a_j)^{.5} \qquad (3.3.3)$$

$$b_{ij} = (1-l_{ij}) (b_i b_j)^{.5} \qquad (3.3.4)$$

where k_{ij} and l_{ij} are empirically determined binary interaction coefficients. The value for b_{ij} is often taken as the arithmetic mean of b_i and b_j.

Finding the location of the critical point in a binary mixture is somewhat more complicated than in a one - component system. A binary critical point is defined by [3.3]

$$\left[\frac{\partial^2 G_m}{\partial x_1^2} \right]_{p,T} = 0 \qquad (3.3.5)$$

17

and
$$\left[\frac{\partial^3 G_m}{\partial x_1^3}\right]_{p,T} = 0 \qquad (3.3.6)$$

The independent variables associated with the Gibbs energy are pressure and temperature. In dealing with supercritical fluids, whether theoretically or in the laboratory, it is more common to have volume and temperature as the independent variables. Most empirical equations of state, for instance, are pressure explicit i.e. pressure is expressed as a function of volume and temperature. In the laboratory, it is more likely that the independent variables will be temperature and volume than temperature and pressure since the volume is easily held constant, whereas pressure is not. For these reasons, it is necessary to replace equations 3.3.5 and 3.3.6 with equations in terms of the Helmholtz energy, A, which is a function of temperature and volume.

Initially, the two components are regarded as separate perfect gases. The Helmholtz energy of the system is $A^+(T,V^+)$ where V^+ is the volume corresponding to this state. When the gases are mixed, the contribution to the Helmholtz energy is

$$A_{mix} = -T\Delta S_{mix} = RT(n_1 \ln x_1 + n_2 \ln x_2) \qquad (3.3.7)$$

where ΔS_{mix} is the entropy of mixing, and n_1 and n_2 are the numbers of moles of the two components.

When the gas mixture is isothermally compressed to the final volume V, the contribution to the total Helmholtz energy

18

is

$$A_{comp} = - \int_{V^+}^{V} p\,dV \qquad (3.3.8)$$

The total Helmholtz energy is thus

$$A(T,v) = A^+(T,V^+) + RT(n_1 \ln x_1 + n_2 \ln x_2) - \int_{V^+}^{V} p\,dV \qquad (3.3.9)$$

The equation of state to be used must therefore be integrated and substituted into the last term of equation 3.3.9. By using the Van der Waals equation, the expression for A becomes

$$A(T,V) = A^+(T,V^+) - nRT \ln\left[\frac{V-b^*}{V^+ - b^*}\right] - a^*\left[\frac{1}{V} - \frac{1}{V^+}\right]$$

$$+RT \ln(n_1 \ln x_1 + n_2 \ln x_2) \qquad (3.3.10)$$

where $a^* = an^2$, $b^* = bn$, and n is the total number of moles.

The critical conditions (equations 3.3.5 and 3.3.6) can then be replaced by the following expressions

$$A_{2V}A_{2x} - A_{Vx}^2 = 0 \qquad (3.3.11)$$

$$A_{3x}A_{2V}^2 - 3A_{2Vx}A_{Vx}A_{2x} + 3A_{V2x}A_{Vx}^2 - A_{3x}A_{2V}A_{Vx} = 0 \qquad (3.3.12)$$

where the subscripts V and x denote partial differentiation of A with respect to V_m and x_1 respectively with the notation from Rowlinson [3.4], $A_{nxmV} = (\partial^{n+m}A/\partial x^n \partial V^m)_T$. The derivatives are obtained from equation 3.3.10.

Van Konynenburg and Scott [3.5] solved equations 3.3.11

and 3.3.12 simultaneously, apparently after much algebra, and predicted the critical point as a function of composition for several binary mixtures.

3.4 Solubilities of solutes

Perhaps the most important aspect of the thermodynamics of supercritical fluid extraction is the solubility of solutes. The extraordinary variation of solubility of a solute with pressure near the solvent's critical point first led to the idea that supercritical extraction could be a useful separation technique.

There have been several attempts to explain the observed solubilities. This section outlines some of the methods used, as well as discussing the solvatochromic effect, which can be used to predict the relative solvating power of solvents.

(a) Ideal

According to Dalton's law, we would expect that the mole fraction of a solute (subscript 2) in a gas is simply the ratio of its vapor pressure to the the total pressure;

$$y_2^o = p_2^{sat}/p \qquad (3.4.1)$$

where y_2^o is the mole fraction of the solute, p_2^{sat} is the saturation vapor pressure of the solute, and p is the system pressure. The solubility of solutes at high pressures, however, is often several orders of magnitude higher than that predicted by this simple relation.

(b) Enhancement factors

Solubilities are often stated in terms of the enhancement

factor, E

$$E = y_2/y_2^o \qquad (3.4.2)$$

where y_2 is the mole fraction of the solute at the given conditions.

The solubility of a solid solute in a fluid at high pressure can be calculated provided that we know the fluid phase fugacity coefficient of the solute. To find the solubility, we first assume that the solubility of the fluid in the solid is negligable. Thus, the condensed phase is pure, and the only non-ideal behaviour is of the fluid phase.

At equilibrium, the fugacity of the solute will be the same in the solid and fluid phases;

$$f_2^S = f_2^F \qquad (3.4.3)$$

The fugacity of the solid phase can be found from

$$RT \ln \frac{f_2^S}{p} = \int_0^P \left[V_2 - \frac{RT}{p} \right] dp \qquad (3.4.4)$$

where V_2 is the molar volume of the solute in the fluid phase. The integral can be separated into two integrals, one from zero pressure to the saturation vapor pressure of the solid, the other from there to the system pressure;

$$RT \ln \frac{f_2^S}{p} = \int_0^{p_2^{sat}} \left[V_2 - \frac{RT}{p} \right] dp + \int_{p_2^{sat}}^P \left[V_2^S - \frac{RT}{p} \right] dp \qquad (3.4.5)$$

where V_2^S is the molar volume of the pure solid solute.

22

Equation 3.4.5 can be rearranged to give

$$f_2^s = p_2^{sat} \varphi_2^{sat} \exp \left[\int_{p_2^{sat}}^{p} \frac{v_2^s}{RT} dp \right] \qquad (3.4.6)$$

where φ_2^{sat} is the fugacity coefficient of the saturated vapor of the solid solute. Thus, φ_2^{sat} corrects for deviations of the saturated vapor of the pure solid solute from ideality. The exponential factor is usually called the Poynting correction, and accounts for the fact that the saturation vapor pressure of the pure solid solute is itself a function of pressure. If the solid solute is essentially incompressible, the Poynting correction is simply

$$\exp \left[\frac{v_2^s (p - p_2^{sat})}{RT} \right] \qquad (3.4.7)$$

The fugacity of the solute dissolved in the fluid phase is

$$f_2^F = \varphi_2^F y_2 p \qquad (3.4.8)$$

where φ_2^F and y_2 are the fluid phase fugacity coefficient and mole fraction of the solid, respectively. Equations 3.4.3, 3.4.6 and 3.4.8 are combined to yield

$$y_2 = \frac{p_2^{sat}}{p} \left\{ \frac{\varphi_2^{sat}}{\varphi_2^F} \exp \left[\int_{p_2^{sat}}^{p} \frac{v_2^s}{RT} dp \right] \right\} \qquad (3.4.9)$$

It is immediately apparent that the enhancement factor is the quantity in the parentheses in equation 3.4.9.

23

If the solid solute is relatively non-volatile, then p_2^{sat} is small and thus φ_2^{sat} is nearly unity. The Poynting correction is usually less than about 3. However, φ_2^F can be considerably less than unity, and thus enhancement factors of 10^3 are not uncommon.

To evaluate equation 3.4.9 requires, among other things, values for the fugacity coefficient of the solute in the fluid phase. Unlike equation 3.4.4, which is only for a pure substance, the fugacity of a substance in a fluid mixture requires information on the volumetric behaviour of the system, usually an equation of state. For a pressure explicit equation of state (e.g. Van der Waals or Peng-Robinson) the fugacity coefficient of the solute in the fluid phase can be found from;

$$RT \ln \varphi_2^F = \int_V^\infty \left(\left[\frac{\partial p}{\partial n_2} \right]_{T,V,n_1} - \frac{RT}{V} \right) dV - RT \ln z$$

(3.4.10)

where z is the compressibility factor of the mixture, and where the partial differential of pressure with respect to n_2 must be evaluated from the equation of state.

Using equations 3.4.9 and 3.4.10, it can be shown that the solubility is expected to go through a minimum, then a maximum as the pressure is increased. At low pressure, the fluid phase phase is nearly ideal, and the solubility

24

decreases with increasing pressure (equation 3.4.1). As the pressure increases, the fluid becomes less ideal, φ_2^F decreases, hence the solubility increases. At high pressures (hence high densities), repulsive forces between the solute and solvent molecules dominate, and the solubility decreases, resulting in a maximum.

Kurnik et al [3.6] demonstrated that the solubilities of several low-volatility solids in supercritical CO_2 could be adequately described using equation 3.4.9 coupled with the Peng-Robinson equation of state. Fitting of the binary interaction coefficient k_{ij} (see equation 3.3.3) was necessary.

The above methods for predicting solubilities are not always successful, due to the fact that supercritical solutions are far removed from an ideal reference state, thus necessitating empirical correlations of the interaction coefficients. The attraction constant in Van der Waals' like equations of state is usually calculated from critical data, but since the critical points of the solvent and solute are often far apart, corresponding states theory does not usually yield an accurate value for the constant. Wong et al [3.7] calculated the unlike interaction parameter from molecular volumes alone, which could be calculated rigorously from pure component properties. The result was a more accurate prediction of solubility isotherms.

Ebeling and Franck [3.8] proposed that the virial equation of state can yield the enhancement factor;

$$\ln E = (V_2^S - 2B_{12})/V^F \qquad (3.4.11)$$

where B_{12} is the mixed second virial coefficient and V^F is the molar volume of the fluid phase.

The above outline and examples indicate that the enhancement factor is easily obtained if volumetric data or a pressure explicit equation of state is available. A volume explicit equation of state, however, can yield the enhancement factor also. For such an equation of state, the fugacity coefficient of the solute in the fluid phase can be found from

$$RT \ln \varphi_2^F = \int_0^P \left(\left[\frac{\partial V}{\partial n_2} \right]_{T,p,n_1} - \frac{RT}{p} \right) dp \qquad (3.4.12)$$

The partial differential of volume with respect to the moles of solute is simply the partial molar volume of the solute in the fluid phase, which can be measured by methods not requiring an equation of state. For instance, Eckert et al [3.9] determined partial molar volumes in supercritical systems based on the variation of density with composition.

The effect of pressure on the fugacity coefficient is thus directly related to the partial molar volume of the solute, $\bar{v}_2$;

$$\left[\frac{\partial \ln \varphi_2^F}{\partial p}\right]_{T,n_2} = \frac{\bar{v}_2}{RT} - \frac{1}{p} \qquad (3.4.13)$$

Experimental data shows that near the critical point of the solvent, the partial molar volumes of solutes are large and negative. The fugacity coefficient of the solute, and hence its solubility, are thus very sensitive to changes in pressure. This fact allows selective extraction and for recovery of the solvent in a supercritical extraction process by reducing the pressure.

(c) Expanded liquid

Mackay and Paulitis [3.10] determined the solubility of non-volatile solutes in supercritical solvents by treating the supercritical fluid as an expanded liquid. The fluid fugacity of the solute is thus

$$f_2^F = y_2 \gamma_2 f_2^{oL}(p_o) \exp \left[\int_{p_c}^{p} \frac{V_{2,m} dp}{RT} \right] \qquad (3.4.14)$$

where y_2 is the solute mole fraction, γ_2 its activity coefficient, and f_2^{oL} is the fugacity of the pure liquid solute evaluated at some reference pressure p_o.

If the reference pressure p_o is chosen to be p_c, then the activity coefficient at infinite dilution, γ_2^∞, and the partial molar volume at infinite dilution, $\overline{v}_{2,m}^\infty$, can be used, since the solute concentration is fairly low. Thus,

$$f_2^F = y_2 \, {}_2 f_2^{oL}(p_c) \exp \left[\int_{p_c}^{p} \frac{\overline{v}_{2,m}^\infty dp}{RT} \right] \qquad (3.4.15)$$

$\overline{v}_{2,m}^\infty$ can be evaluated from the desired equation of state using

$$\overline{v}_{2,m}^\infty = \lim_{n_2 \to 0} \left[\frac{\partial V}{\partial n_2} \right]_{T,p,n_1} \qquad (3.4.16)$$

The fugacity of the condensed phase of the solute is

$$f_2^C = f_2^{oS}(p_c) \exp \left[\int_{p_c}^{p} \frac{v_{2,m}^C dp}{RT} \right] \qquad (3.4.17)$$

At equilibrium, the fugacities of the solute in the fluid and

28

solid phases must be equal. Thus, from equations 3.4.15 and
3.4.16 the solute mole fraction is

$$y_2 = \frac{f_2^{os}(p_c) \exp\left[\dfrac{v_{2,m}^c(p-p_c)}{RT}\right]}{\gamma_2^{\infty}f_2^{oL}(p_c) \exp\left[\displaystyle\int_{p_c}^{p} \dfrac{v_{2,m}\,dp}{RT}\right]} \tag{3.4.18}$$

The ratio of the fugacities of the solute in the solid and
liquid forms can be approximated by

$$\ln\left[\frac{f_2^{os}(p_c)}{f_2^{oL}(p_c)}\right] = \left[\frac{H_{fus,2}}{R}\right]\left[\frac{1}{T_{m,2}} - \frac{1}{T}\right] \tag{3.4.19}$$

where $H_{fus,2}$ and $T_{m,2}$ are the heat of fusion and normal
boiling temperature of the solute respectively. The value of γ_2^{∞}
is found from experimental solubility data.

(d) Equilibrium

One of the simpler methods to relate solubilities to
temperature and pressure was detailed by Chrastil [3.11],
where k solvent molecules (B) are assumed to be in equilibrium
with one solute molecule (A) by forming a solvato complex;

$$A + kB \rightleftharpoons AB_k \tag{3.4.20}$$

The equilibrium constant for the reaction can then be written

$$K = \frac{[AB_k]}{[A][B]^k} \tag{3.4.21}$$

29

which can be rearranged to give

$$\ln K + \ln[A] + k \ln[B] = \ln[AB_k] \qquad (3.4.22)$$

The equilibrium constant K can be expressed as

$$\ln K = - \Delta H_{solv}/RT + q_s \qquad (3.4.23)$$

where ΔH_{solv} is the enthalpy of solvation and q_s is a constant. The vapor concentration of the solute can be found from the Clausius – Clapeyron equation, assuming that the solute is at a temperature well below its critical temperature

$$\ln[A] = -\Delta H_{vap}/RT + q_v \qquad (3.4.24)$$

where ΔH_{vap} is the heat of vaporization of the solute, and q_v is a constant. Assuming $[A] << [AB_k]$, we get

$$\Delta H/RT + q + k \ln[B] = \ln[AB_k] \qquad (3.4.25)$$

where ΔH is the total heat of reaction, $\Delta H_{solv} + \Delta H_{vap}$, and $q = q_s + q_v$. Note that we have assumed ΔH_{solv} and ΔH_{vap} are not functions of temperature themselves.

We may then write

$$[AB_k] = c/(MW_A + kMW_B) \qquad (3.4.26)$$

and
$$[B] = \rho/MW_B \qquad (3.4.27)$$

where c is the solute concentration in g L^{-1}, ρ is the density of the gas in g L^{-1}, and MW_A and MW_B are the molecular weights of the solute and gas, respectively. Thus, from equation 3.4.25, we get

$$\Delta H/RT + q + k \ln \rho - k \ln MW_B = \ln c - \ln(MW_A + k MW_B)$$
$$(3.4.28)$$

30

which can be expressed as

$$c = \rho^k \exp(a/T + b) \qquad (3.4.29)$$

where $a = \Delta H/R$ and $b = \ln(MW_A + k\, MW_B) + q - k \ln MW_B$.
Therefore, a plot of ln c versus ln ρ will have a slope of k,
and an intercept of $a/T + b$.

The most striking feature of equation 3.4.29 is that the
solubility of the solute is seen to increase with solvent
density, a phenomenon seen in practice. Furthermore, the
solubility decreases as temperature increases. (The equation
of state may be used to predict the variation of density with
temperature and pressure.) Chrastil determined the constants
of equation 3.4.29 for several experimental systems.

Adachi and Lu [3.12] extended the work of Chrastil by
considering the quantity k to be a function of density.

(e) Solvatochromic effect

Kamlet, Abboud and Taft [3.13] developed a solvent scale
based on the effect of the solvent polarity/polarizability on
the π^* electronic transition of a solute probe molecule
(often 2-nitroanisole). The probe molecules selected by Kamlet
et al have π^* electronic states that are more polar than the
ground state. A change in the polarity of the solvent changes
the electronic gap, thus changing the position of the
absorption band.

An empirical relationship was derived between the

31

measured solvent absorption maximum and the polarity of the
solvent:

$$\nu = \nu_0 + s\pi^*$$ (3.4.30)

where ν is the absorption maximum in the test solvent, ν_0 is
the absorption maximum in the reference solvent, s is a solute
dependent parameter, and π^* is the measured solvent polarity
parameter.

The solvatochromic behaviour of a probe molecule (2-
nitroanisole) in the carbon dioxide + 2-propanol system was
investigated by Yonker and Smith [3.14]. The cybotactic region
of the solute probe molecule (the region of solvent molecules
whose structure is influenced by the solute) was found to be
highly enriched in 2-propanol. This type of investigation
should provide a greater understanding of the molecular
structure of supercritical fluids.

4. Experimental data for binary SCF systems

4.1 Classification of systems

Although SCF solvent extraction processes of interest to the analytical chemist would likely involve multicomponent mixtures, most systems can be adequately described by considering only binary mixtures.

The phase rule of Gibbs is

$$F = C - P + 2 \qquad\qquad (4.1.1)$$

where F is the number of independent variables, C is the number of components, and P is the number of phases in the system. Thus, for a two-component one phase system (C=2, P=1), there can be a maximum of three independent variables. A binary system, therefore, can be completely described by a three dimensional phase diagram involving pressure, temperature, and the mole fraction of one component. (Alternatively, the molar volume could be used in place of one of these variables.) In such a "pTx" diagram, one phase is represented by a volume, equilibrium between two phases by two surfaces, and equilibrium among three phases by lines, i.e. intersections of two phase surfaces. Also, the diagrams show equilibrium lines between two phases of a single component and critical lines of mixtures.

A simple pTx diagram for a class I binary mixture (the classes of binary mixtures are explained below) is shown in

33

figure 4.1a. The two solid lines represent the vapor liquid equilibria for the two components, and terminate at their respective critical points. The dotted line joining the critical points is the locus of critical points of mixtures of the two components. Three constant temperature planes through the two surfaces representing gas-liquid equilibria are also shown.

A somewhat simpler method to present some of this information is to plot a projection of the three dimensional pTx diagram on a two dimensional diagram. For instance, figure 4.1b is a pT projection of the gas-liquid equilibrium lines and critical locus of figure 4.1a. This type of projection is used to classify the various types of binary phase diagrams (see below).

Figure 4.1c is a px diagram showing two of the constant temperature planes shown in figure 4.1a. Tie-lines relating the coexisting gas and liquid phases run horizontally. The critical locus curve is shown, emphasizing that the critical pressure of a binary mixture is not simply a linear function of the composition.

Based on px projections, binary mixtures can be grouped into six classifications [3.4]:

Class I. The two critical points are joined by a continuous

34

line, and there is complete miscibility of the liquid phases at all temperatures (figure 4.2a).

Class II. Similar to class I, but there is liquid-liquid immiscibility at low temperatures, and the upper critical solution temperatures (UCSTs) are distinct from the gas-liquid critical line. The lower bound of the UCST line is the intersection with a three phase liquid-liquid-gas equilibrium line (figure 4.2b).

Class III. There is no continuous gas-liquid critical line. There is, however, another critical line originating at C_1 and ending at the critical endpoint K, where it intersects a liquid-liquid-gas equilibrium line (figure 4.2c).

Class IV. The critical point C_2 is joined by a critical curve to the lower critical endpoint at the intersection with a liquid-liquid-gas equilibrium line. A second critical curve is similar to that described for class III mixtures. As in class II mixtures, the UCSTs are distinct from the critical line (figure 4.2d).

Class V. Similar to class IV mixtures, but without the region of liquid-liquid immiscibility at lower temperatures. Also the liquid-liquid-gas equilibrium line is often fairly short, so that class IV mixtures may be similar to class I mixtures (figure 4.2e).

Class VI. The triple point temperature of one pure component

is much greater than the critical temperature of the second component, and the critical curves intersect solid-liquid-gas equilibrium lines at the upper and lower critical endpoints. At temperatures between the endpoints, solid-gas equilibrium exists to very high pressures (figure 4.2f).

The six classifications described above can be calculated [3.5] using an equation of state such as Van der Waals'.

There are other mixtures which exhibit phenomena such as low temperature LCSTs. This low temperature behaviour results from strong interactions between molecules, rendering simple equations of state unable to describe the system.

4.2 Some examples of binary systems

Some examples of each class of binary mixture are presented in table 4.1. The usual criteria for a mixture being a class I type are that the two components are of similar chemical type, and that their critical properties are similar. Some examples are $CO_2 + O_2$, $CO_2 + C_2H_6$, benzene + toluene and Ar + Kr. Although most class I mixtures have critical lines with the shape shown in figure 4.2a, the critical line may be almost flat, when the critical properties of the two components are almost identical ($CO_2 + N_2O$ for instance). The curve may exhibit minima, indicative of weak intermolecular interactions, and large deviations from Raoult's law. This occurs with mixtures of aromatic hydrocarbons with aliphatics. Some additional examples are $C_2H_6 + HCl$, and methanol + benzene.

There are some systems where the curve passes through temperature and pressure maxima greater than the critical temperature of either component. This implies partial immiscibility of the two components, and since the conditions are supercritical, this must be considered fluid-fluid immiscibility (often called gas-gas immiscibility).

There are also binary systems of class I whose critical lines are not smooth curves between the two critical points.

Type II binary mixtures show some liquid-liquid

37

immiscibility below the critical temperature of the more volatile component. The pressure-mole fraction diagrams of class II systems may be subdivided as described by Rowlinson and Swinton [3.4]. However, for the purposes of supercritical extraction, it is unlikely that the conditions will be chosen such that a liquid phase is present, hence the region of liquid-liquid immiscibility is not of interest. Some systems which belong to class II are CO_2 + n-heptane, n-pentane + nitrobenzene, water + phenol, methanol + cyclohexane and acetic acid + trimethylamine.

The critical curve of class III mixtures does not always correspond to that shown in figure 4.2c. For instance, the curve may also go through a pressure minimum, followed by a pressure maximum (e.g. ethane + methanol). Other examples of class III behaviour are CO_2 + large alkanes and nitrogen + ammonia. Many class III mixtures exhibit fluid-fluid immiscibility, including argon + ammonia, methane + ammonia, and carbon dioxide + water.

Class IV and class V have, as described above, a critical line that joins the gas-liquid critical point of the less volatile component with the lower critical endpoint at the intersection with a liquid-liquid-gas line. It is instructive to note then, that the nature of the locus of points changes continuously from gas-liquid to liquid-liquid, and hence one

38

must be careful in the use of the words gas and liquid in the critical region. Typical examples of class IV systems are CO_2 + nitrobenzene and methane + 1-hexene. Class V behaviour is found in mixtures of ethane with ethanol, 1-butanol, and 1-propanol.

Class VI behaviour is seen only in systems where there is hydrogen bonding between the two components, or in one of the pure components. One of the components is usually water. An example is water + 2-butanone.

5. Use of Co-solvents

5.1 Effects of co-solvents on extraction

The solubility of a solute in a one component supercritical solvent was discussed in section 3.4. As discussed in chapter 4, however, the critical properties of a mixture are quite different from those of the pure solvents, and thus one would expect that the solubilities of solutes can be changed markedly by changing the composition of the solvent. In the case of supercritical extraction, the solvent might be chosen to provide the highest possible extraction efficiency of a certain solute, or to exclude the extraction of another.

A two-component solvent in addition to a solute is a ternary system. It is much more convenient, however, to treat the two-component solvent as a single fluid with a dissolved solute. (This may not be possible if the co-solvent or the solute have appreciable mole fractions.) The solvent component with the smaller mole fraction is referred to as the co-solvent, modifier or entrainer.

The use of a co-solvent can benefit extraction processes in one of four ways [5.1,5.2];
(a) The solubility of the substances to be extracted may be enhanced.
(b) The temperature and pressure dependence of the

solubilities of low volatility substances may be more
pronounced than without a co-solvent. This may increase the
selectivity and enable solvent regeneration merely by
increasing the temperature.

(c) The separation factors between the solvent and the matrix
to be extracted can be specifically influenced. This fact may
be used to increase the selectivity of extraction.

(d) The co-solvent can be used as a reactive component. Sunol
[5.2] has suggested that a co-solvent in supercritical fluid
extraction could be used to desulphurize coal, for instance.

Although solubility is not the only factor controlling
the efficiency of extraction, it is probably one of the most
important. As was demonstrated in section 3.4, solubility
generally increases with increasing density, so that the first
function of a co-solvent would be to increase the density of
the fluid phase. Figure 5.1 shows how the critical density of
CO_2 - hydrocarbon mixtures increases as the mole fraction of
the hydrocarbon is increased [5.3]. Solubility is also related
to the polarity/polarizability of the solvent, which can be
quantified as discussed earlier.

Schmitt and Reid [5.4] proposed that the entrainer acts
as a second solvent in a solvent mixture, rather than simply
changing the supercritical fluid density.

An important use of co-solvents has been in supercritical

41

fluid chromatography, in analogy with the practice in liquid chromatography. For example, the addition of small amounts of methanol (1-5%) to the mobile phase leads to much improved peak shapes and reduced retention times for some polar compounds. It is not clear whether this is due to the increase in polarity of the solvent, or due to selective adsorption of the co-solvent molecules on strong adsorption sites on the stationary phase. There is evidence that the latter effect is the dominant one [5.5]. Levy and Ritchey [5.6], however, demonstrated the utility of different co-solvents in the chromatography of various solutes. Separation factors, peak shapes and retention times were all affected by the choice of co-solvent for a particular solute. In general, the co-solvents with the largest capability for hydrogen bonding with the solutes had the largest effects. Proplylene carbonate, for instance, provided the fastest elution times for most of the solutes studied.

Walsh et al [5.7] found that the co-solvent effect is due to a chemical association between the solute and co-solvent molecules, and presented a model that accounts for these associations. They also showed that spectroscopic and solvatochromic methods can be used to make qualitative predictions of the co-solvent effect in a supercritical fluid. Various systems were analyzed in terms of their Lewis acid-

base properties, and the associations were shown to be due either to hydrogen bonding or to the formation of charge-transfer complexes. For example, in the system carbon dioxide-methanol-acridine, the high enhancement factor of acridine was explained by the affinity of the Lewis acid methanol for the Lewis base acridine.

Dobbs [5.8] predicted solubilities and selectivities in solvent-co-solvent mixtures from a model which treated the effects of dispersion forces, orientations of the molecules involved, and hydrogen bonding on solubility enhancement.

5.2 Likely Solvent Mixtures for SFE

Although the solvent chosen for an extraction must depend
on the species that are to be extracted, some generalizations
are possible. Carbon dioxide is the most popular supercritical
fluid for a number of reasons. It is non-toxic (important for
extraction of food-related compounds), non-flammable,
inexpensive, and its critical pressure and temperature are
easily attained. For the laboratory extraction of organics
from solid matrices, however, these properties may not be
necessary. Other solvents which have some or all of these
properties are nitrous oxide, sulfur hexafluoride, xenon and
some of the lower alkanes. Possible co-solvents include
methanol, propanol, tetrahydrofuran, diethyl ether, dimethyl
sulfoxide, water, ammonia, propylene carbonate, dioxane,
acetonitrile, and methylene chloride. These compounds are
relatively polar, but could not be used alone due to their
high critical temperatures and/or pressures. (The compounds
which are gases at ambient temperature would need to be
liquefied before being pumped up to supercritical conditions.)

Brunner [5.9] has divided extractions into three general
cases to allow the proper choice of mixed solvent. The three
cases differ with respect to the concentration of solute that
can be achieved in the supercritical solvent. In the first
case, the desired compounds are the only ones that dissolve in

the solvent. Thus, the solvent would be chosen solely to achieve the maximum solubility possible. In the second case, all compounds dissolve in the solvent, but to considerably different degrees. Again, the solvent would be chosen to maximize solubilities, since some separation of desired from undesired compounds is readily achievable. Knowledge of the phase behaviour will be necessary to choose the optimum operating conditions. In the third case, all the extractable compounds are soluble to the same extent in the solvent. Here, the separation factor is more important than the solubilities. Again, the phase behaviour of the system will be necessary to choose the appropriate co-solvent.

To simplify the procedure for choosing an co-solvent, Brunner recommends that the critical temperature of the co-solvent be higher than the intended extracting temperature, otherwise the reduced temperature of the co-solvent will be high, hence the solvent system density will be low.

The selective extraction of organic species has been reported [5.10] using pure CO_2 as well as $CO_2+5\%$ methanol. Separation of alkanes from polycyclic aromatic hydrocarbons was successful.

6. Computer prediction of SCF properties

6.1 Critical temperature and pressure of pure compounds

The critical temperature and pressure of a pure substance may be estimated using only the normal boiling point and the molecular structure. For organic substances, Soulie and Rey [6.1] detail a method based on the contributions of atoms or groups of atoms to the difference in internal energy between a real and a perfect gas. The method is somewhat empirical, and so is not very accurate, but is sufficient to at least estimate the critical constants. Some estimated values of T_c and p_c calculated by this method for various solvents are given in table 6.1.

6.2 Densities

Using a computer and an appropriate equation of state, the variation of density with temperature and pressure of any solvent system can be calculated. One need only know the critical constants for the individual components. As shown in figure 3.3, the Peng-Robinson equation of state gives reasonable predictions of solvent density above the critical point. Using the fact that the critical compressibility factor for a Peng-Robinson fluid is 0.307, the critical densities for several single solvents were calculated, and are presented in table 6.2 along with the critical temperatures and pressures. There is a wide range of critical densities, from the order of 100 g dm^{-3} to 1000 g dm^{-3}.

Using the mixing rules in equations 3.3.1 to 3.3.4, an equation of state may also be used to predict the densities of multicomponent systems. A listing of a computer program written by one of the authors (R.C. Burk) to predict the densities of binary systems using the Peng-Robinson equation of state is given in Appendix III. The inputs required from the user are the critical temperature and pressure, molecular weight and acentric factor of each component. The program will then generate a table of density versus pressure at a specified temperature. Plots of the density at 90 $^{\circ}$C of the system carbon dioxide + n-butane versus pressure calculated by

47

the program are given in figure 6.1. The density increases as the mole fraction of n-butane decreases, until the curves cross at roughly 27 MPa. Above this pressure, decreasing the mole fraction of n-butane actually decreases the solvent density. Plots such as this would be useful in determining the optimum pressure and mole fraction of co-solvent to be used in an extraction. Figure 6.2 shows the variation of density with pressure for a system of carbon dioxide + 5% n-butane at different temperatures. As expected, the density at a given pressure becomes lower as the temperature is increased.

The exact variation of density with pressure cannot be calculated with an equation of state since the mixing rules are somewhat arbitrary. The fit is much better, however, if the (empirically determined) interaction coefficients are known. Use of more complex equations of state containing more terms only complicates the matter, since the mixing rules become cumbersome.

The binary interaction coefficients k_{ij} and l_{ij} in equations 3.3.3 and 3.3.4 were set to 0.13 and 0.0 respectively for the calculations involving carbon dioxide + n-butane, as suggested by Peng and Robinson [3.2].

7. Extraction methods for trace organics

7.1 Current methods

The extraction methods specifically for polycyclic aromatic hydrocarbons (PAH) will be briefly reviewed in this section, since this class of compounds has generated considerable interest with respect to environmental solids.

Most quantitative determinations of PAH on a solid matrix require a preliminary extraction step, since few sample matrices are amenable to direct analysis without serious interferences. Some matrices require only a single and simple extraction, whereas others require more complex extraction schemes as well as enrichment procedures to further concentrate the PAH.

Jacob and Grimmer [7.1] have summarized the procedures for extraction of PAH from a variety of matrices. The matrices are divided into six groups, as shown in table 7.1. The general categories of matrices vary from those which are soluble in the extracting solvent (vegetable and fuel oils, for instance) to those which are insoluble (such as graphite). The extraction procedure and solvent required vary considerably from one matrix to the next. For soluble matrices, a single extraction with cyclohexane is sufficient to quantitatively solubilize the PAH. The resulting solution can then be subjected directly to any necessary enrichment

49

procedures.

Where the matrix is a liquid that is immiscible with the extraction solvent, the extraction is characterized by a liquid-liquid distribution, and so depends strongly on the choice of solvent. This procedure is used to analyze water samples for PAH. Another method for water analysis is to first adsorb the PAH onto a sorbent material (the pre-extraction step) and then extract the PAH from the sorbent material using a liquid solvent.

Many food and biological materials are not soluble, or only partly soluble, in common extraction solvents. In such cases, extraction may be preceded by saponification with KOH or NaOH to yield a soluble matrix. Materials which are resistant to saponification can be mechanically homogenized, then extracted with, say, acetone.

Jacob and Grimmer recommend that heterogeneous materials containing inorganic material (dusts, soils, and sewage sludge, for instance) be first extracted with acetone, then with xylene if the acetone extraction is incomplete.

Finally, graphite-like materials require repeated extraction with boiling xylene, since the PAH may be partly innaccessible to the solvent due to the "cage" effect.

Griest and Caton [7.2] reviewed the extraction of PAH from several matrices for quantitative analysis. The methods

reviewed were solvent extraction, thermal methods (sublimation from solid matrices and distillation from liquid ones), and extraction by preconcentration onto solid phases. Some general precautions for PAH extraction were identified:

(i) To avoid contamination, all equipment used in the extraction should be extracted itself beforehand.

(ii) Solvents used should be of high purity and freshly redistilled before using.

(iii) Samples should be extracted promptly after collection to avoid degradation and/or sublimation of the PAH.

(iv) The extraction temperature should be kept to a minimum to prevent loss of volatile PAH components.

(v) An internal standard, itself a PAH, should be employed to allow calculation of extraction recoveries. (Jacob and Grimmer [7.1] recommend using two internal standards; one added before extraction, and one during the subsequent enrichment procedure.)

Lee and Schuetzle [7.3] summarized the sampling, extraction, and analysis of PAH from engine soots. They categorized extractions according to the two most popular methods, namely Soxhlet extraction and ultrasonic agitation. These two techniques make up the majority of extractions of environmental solids such as dust, soot, fly ash and marine

51

and freshwater sediments. The Soxhlet procedure has been specified by various agencies and committees as a standard reference method [7.2]. There are, however, several "standard" methods for the same matrix which differ considerably in such details as choice of solvent, extraction time, and the number of solvent cycles.

7.2 Supercritical methods

Several authors have reported the extraction of trace organic compounds from various matrices. Paulaitis et al [7.4] reviewed experimental studies up to 1983 in which a solid phase was contacted with a supercritical fluid phase. Most of the solids were organics, and the solvent of choice was usually CO_2. Other solvents, notably H_2O, C_2H_4, He, and Ar, have also been used. Also tabulated by Paulaitis were data from extractions of liquids by supercritical fluids. For most of the systems reported, however, the aim was to obtain phase equilibrium data, and not to extract the solid from a matrix.

Hawthorne and Miller [5.10,7.5] used supercritical CO_2 and N_2O to extract PAH from environmental solids, and from sorbent traps. A later publication by the same authors [7.6] detailed the extraction of PAH and PCB from solids, but with the extraction directly coupled to gas chromatographic analysis. Wright et al [7.7] used a similar method to desorb PAH from glass beads and from a sample of urban dust. They were also successful in selectively extracting PAH compounds at various pressures, and in showing that the entire extraction and analysis system could be automated. Raymer and Pellizzari [7.8] found that the extraction of various chlorinated compounds from a sorbent trap by supercritical CO_2 was much more efficient than thermal desorption methods. They

used radiolabelled compounds, and determined extraction efficiencies by scintillation counting of the extract. Wright et al [7.9] used supercritical CO_2 and isobutane to extract a range of PAH from adsorbent materials.

Schnitzer et al [7.10,7.11] reported the extraction of alkanes and alkanoic acids from soils and humic materials. The solvent polarity, as determined by the amount and nature of the co-solvent added, affected the relative extractions of polar and non-polar compounds. In general, the proportion of aromatic compounds in the extracts increased with increasing solvent polarity, while the proportion of alkanes, alkanoic acids and carbohydrates decreased.

Dooley et al [7.12] extracted DDT from soil samples using supercritical carbon dioxide with methanol and toluene as co-solvents. The CO_2 - methanol system provided the best extraction under the conditions used.

Supercritical extraction of several food materials have been reported [5.1]. Oils from vegetables, including corn, palm, sunflower and hops, and oils from animal sources have been extracted. Much of the oil can reportedly be removed from potato chips. The solvent used for such operations is usually CO_2 due to its non-toxic properties.

Flavor and fragrance compounds were extracted from spices and spruce tree needles [7.13].

The Kerr-McGee Corporation patented a process, originally designed to extract useful products from oil residuums, for solvent extraction in which the solvent is recovered as a supercritical fluid [7.14].

Critical Fluid Systems Incorporated designed a system for extraction of organics from hazardous wastes using near-critical CO_2 [7.15].

The extraction of organic pollutants directly from water using supercritical CO_2 has been reported [7.16].

8. Analytical methods for trace organics

The detection and identification of polycyclic aromatic hydrocarbons can be carried out by UV/VIS spectrometry, fluorometry, thin-layer chromatography, paper chromatography, high performance liquid chromatography, gas chromatography (GC), especially capillary, or gas chromatography combined with mass spectrometry (GC-MS). More recently, the analyses have been done with supercritical fluid chromatography (SFC), or with a combination of supercritical extraction and SFC (SFE-SFC). At present, capillary GC and SFE-SFC afford the best overall performance in terms of resolution and speed of analysis. The other techniques, however, are useful especially when specific methods of detection are employed.

8.1 UV/VIS spectrometry

PAH compounds have characteristic absorption spectra in the ultraviolet and visible regions. Although there are several compilations of spectral data available, it must be remembered that quantitative determinations can seldom be made in mixtures of more than two or three PAH compounds. Interpretation of the spectra can be difficult. For instance, PAH with methyl groups often give UV spectra very similar to those of the parent compounds. Also, the exact position of the absorption bands is dependent on the solvent used. [8.1]

8.2 Fluorometry

Fluorescence spectroscopy of PAH compounds is most often used in conjunction with thin-layer or paper chromatography since measuring fluorescence spectra without prior separation of the compounds is not possible due to interferences. The fluorescence spectra can be recorded directly from the paper, or after first extracting the substances with a suitable solvent.

Fluorescence spectra recorded at very low temperatures (usually that of liquid nitrogen, 77 K) show a number of distinct and narrow lines. This phenomenon is known as the Shpol'skii effect, and has been reported to be useful even in mixtures of PAH compounds.

The main disadvantages of fluorometry stem mainly from the sensitivity of the recorded spectrum to instrumental parameters, solvent or adsorbent (e.g. paper or TLC material), and the presence of quenching substances such as oxygen.

8.3 Paper chromatography

There are three paper chromatography methods that have been successfully applied to the separation of PAH [8.1]:

1. A method employing paper impregnated with N,N'-dimethylformamide (DMF) and using n-hexane saturated with DMF as the mobile phase.

2. Acetylated paper, using either toluene:methanol:water (1:10:1) or methanol:ether:water (4:4:1).

3. Paper impregnated with liquid-paraffin.

Paper chromatography has lagely been replaced by thin-layer chromatography.

8.4 Thin-layer chromatography

Thin-layer chromatography (TLC) uses essentially the same separation system as paper chromatography, with the advantage that smaller amounts can be detected, and the analysis time is much shorter. For the separation of PAH, thin layers of silica gel and alumina are eluted with alkanes or cyclohexane. The separation depends mainly on the number of rings in the compound, and thus isomers are not usually well separated.

8.5 High pressure liquid chromatography

High pressure liquid chromatography (HPLC) is useful for the separation of compounds which have boiling points that are too high or thermal stabilities that are too low for gas chromatography. It has therefore been applied to PAH with considerable success.

HPLC detection is usually by fluorescence, or UV/VIS spectrophotometry. Full spectra may be recorded by collecting fractions, or by using a 'stop and go' technique.

Although the detection capability of HPLC is inferior to that of capillary gas chromatography, this is offset to some extent by the application of specific detection methods.

8.6 Gas chromatography

Gas chromatography (GC), especially capillary GC, has been the method of choice for the analysis of complex mixtures of PAH for some time. The subject has been reviewed extensively [8.2]. Most of the early work on GC analysis of PAH was done using packed columns, but with the advent of durable and highly efficient stationary phases, the capillary column has all but eclipsed the use of packed columns in this area.

There are four major areas where capillary columns have been particularly useful:

1. Resolution of isomers

2. Analysis of complex mixtures

3. Chromatographic "fingerprinting"

4. Fast separations

All of these uses have been proven effective for the analysis of PAH, but it is probably the second one that is of most interest with respect to extraction from environmental solids, as these matrices often have several PAH compounds adsorbed onto them.

The choice of stationary phase in packed column GC has been the subject of much dispute among chromatographers over the years. This choice is not quite so critical with capillary GC, however, because of the much higher resolution afforded by

capillary columns. The stationary phases most often used are SE-52 and SE-54, which are polyphenylmethylsiloxanes.

The carrier gas used is most often helium, although hydrogen has several advantages over helium, including better resolution and shorter analysis time.

There are three common injection methods; splitless injection, on-column injection, and cryogenic trapping. Spiltless injection was probably the most widely used method until the advent of on-column injection, which does not suffer from as much discrimination (the tendency of less volatile compounds to be delayed in the injection system). Cryogenic trapping is based on freezing the solutes out onto the head of the GC column. This has also been used in conjunction with supercritical fluid extraction. [5.10]

The detector used most often in the GC analysis of PAH is the flame ionization detector (FID). Its general response character makes it ideal for several classes of compounds, but also necessitates some kind of sample cleanup if only the PAH are to be detected.

A mass spectrometer is probably the most desirable GC detector for PAH. If a large number of PAH are to be determined, the aid of a computer is indispensible. Each GC peak is scanned several times, and spectra can be stored for subsequent matching with reference library spectra. Low

63

resolution mass spectrometry coupled with high resolution GC can yield acceptable results. Interpretation of GC-MS results can be enhanced if coupled with UV/VIS results.

8.7 Supercritical fluid chromatography

Supercritical fluid chromatography is analogous to conventional GC, in that separation is carried out within a capillary column coated with a stationary phase. However, in SFC, the mobile phase is not a gas, but a supercritical fluid. Solutes that are beyond the volatility range of GC, or that are thermally labile can be analyzed by SFC in less time and at higher efficiencies than by HPLC. The resolution of capillary SFC is comparable to that of capillary GC.

Since there is a direct relationship between the solubility of solute and the density of a supercritical fluid (see section 3.4), programmed ramping of the fluid density is used to extend the molecular weight range and to allow the separation of complex mixtures.

A variety of mobile phases can be used in SFC. Carbon dioxide is most often used, but nitrous oxide, or ammonia can be used when a more polar mobile phase is required (for instance when separating polar compounds such as drugs and their metabolites). There has been much interest recently in the addition of modifiers to the mobile phase (e.g. methanol) to improve selectivities.

One of the major advantages of SFC is that both GC and HPLC detectors can be used. The detector most often used appears to be the flame ionization detector. SFC has also been

coupled to mass spectrometers.

Several manufacturers now offer an SFE-SFC system, which is essentially a supercritical extraction system connected to a supercritical fluid chromatograph. These systems consist of an extraction vessel, an accumulator, where the extracted solutes are concentrated, and a valving system for admitting the extract to the chromatographic column. The advantage of these systems is that the extract is not handled by the operator, but is transferred directly from the extraction vessel to the chromatographic column.

9. SCF Extraction Apparatus

9.1 Solvent preparation

For most supercritical extraction studies, the solvent used is carbon dioxide, possibly with a small amount of a co-solvent such as methanol. Usually, the solvent is used as received, without further purification.

Kay and Kreglewski [9.1] degassed benzene by first percolating it over activated silica gel to remove water, then freezing it and pumping off the non-condensable gases. It was then transferred by distillation to a refrigerated storage flask.

9.2 Pumps

Pumps used in supercritical extraction were originally developed for high performance liquid chromatography. There are several manufacturers, each with a few models differing in such variables as the volume displaced by a full stroke, the flow rate range, and the maximum pressure.

Pumping systems can be broadly classed as either reciprocating or non-reciprocating. The non-reciprocating pumps can be pneumatic or syringe type. The pneumatic pumps use a pressurized gas to drive the liquid phase either directly or through a moving separator to avoid dissolution of the gas in the liquid. Although this type of pump is inexpensive, the maximum pressure is generally limited to 10 MPa, which is insufficient for most supercritical applications. A variation on the pneumatic pump is the pneumatic amplifier pump, which achieves high pressures by having a large area on the low pressure side of the piston compared to the high pressure side. These pumps are capable of much higher pressures, and have been used [9.2] for supercritical extraction and chromatography.

The most common type of non-reciprocating pump is the syringe pump, in which the liquid enclosed in a cylinder is pushed at constant speed by a piston. The main advantage of this type of pump is that the flow rate is constant when

68

equilibrium conditions are established. For supercritical extraction, it must be realized that the volume of the syringe must be sufficient to carry out an entire extraction, since the pump does not refill itself during operation.

Reciprocating pumps rely on the movement of a plunger to draw in the solvent during the back stroke, and to deliver it during the forward stroke. Check-valves ensure the proper flow direction. For liquid chromatography use, these pumps must be fitted with devices to minimize the flow and pressure pulsations. This is not a problem in supercritical extraction however, as long as the extraction chamber is not connected to a chromatographic column. Reciprocating pumps are available with one, two or three heads each with its own flow rate control, and all driven by the same motor. This allows up to three different solvents to be combined in any ratio before entry into the extraction vessel. Colin, Guiochon, and Martin [9.3] have reviewed pumping systems for high performance liquid chromatography.

9.3 Extraction vessels

Extraction vessels may have any one of a multitude of forms, depending on the sample size, temperature and pressure used and the type of experimental data sought. Some essential features of an extraction vessel are:

(a) The vessel must be able to withstand the specified maximum temperature and pressure of the extraction.

(b) The materials of construction must be compatible with the solvents used.

(c) The solvent must be able to enter and exit the vessel, but the sample must be prevented from escaping.

(d) The device must allow easy charging of the sample, and recovery of the residue from extraction.

(e) Allowance must be made for any special features such as optical windows.

Some of the devices which have been reported are a thick walled glass tube [9.1], a short length of stainless steel tubing with standard tubing fittings (approximately 0.5 ml volume) [5.10], tubing fittings themselves [7.1,7.5,7.13], a glass lined cylindrical extraction vessel (approximately 5 ml volume) [7.9], a nickel alloy cylinder equipped with a piston to vary the internal volume (from a few ml to 52 ml), and with a sapphire window for visual observations [9.4]. (Some of these devices were used to study phase equilibria, but their

features could conceivably be used for supercritical extraction vessels.) Schnitzer [7.10,7.11] used a discarded HPLC column for extracting soil samples.

9.4 Pressure let-down devices

There are two basic methods for recovering the analyte from the extract. The more common method is to reduce the pressure to a value below the critical pressure, i.e. flash off the solvent. A less common method is to increase the temperature, causing the solute to precipitate out. This method has some application where the solvent must be re-used, since it is economical not to have to recompress it to supercritical pressures. For laboratory scale work, however, the former method is simpler.

Several devices have been reported which reduce the pressure from supercritical to ambient. Perhaps the simplest is a narrow bore (approximately 25 μm) tube with one end connected to the extraction vessel, and the other end at ambient pressure. With an extraction pressure of 200 atm, a 10 cm length of tubing was said to have a flow rate of approximately 60 ml min^{-1} [5.10]. A frit at the outlet of the extraction cell prevented any of the particulate material of the sample from being carried over into the capillary or the collector vessel.

Another simple device was reported [7.9] which used a short length of narrow bore (50 um) stainless tubing crimped at the outlet end to control the flow rate of fluid and serve as the depressurization zone for the extraction stream. The

flow rate was said to be somewhat variable due to the imprecise nature of crimping the tubing.

A diaphragm with a laser drilled 3 um diameter hole was used as a restrictor for reducing the pressure between a supercritical fluid chromatograph and a mass spectrometer [9.5].

A restrictor can be made from a capillary glass tube sealed at one end, then gently abraded until a hole of specified diameter is formed [9.6].

There are several problems associated with the sudden decompression of the solvent. The sudden pressure drop causes sonic flow conditions with the potential for shock waves, and there is a large temperature drop due to the Joule-Thomson effect. The latter effect was demonstrated to be the cause of low recoveries of analyte, and it was theorized that the sudden cooling caused the analyte to nucleate, become entrained in the gas stream, and be carried away [7.9]. This problem may be solved by sufficient heating of the expansion device, or by proper choice of the solute recovery system, which is discussed in the next section.

9.5 Solute recovery systems

There must be an effective method to collect the sample
after expansion to ambient pressure. Some of the methods
employed include dissolution in a small amount of liquid
solvent [5.9], cryogenic trapping of the entire sample at
liquid nitrogen temperatures followed by evaporation of the
solvent [7.9], and cryogenic trapping of the sample at a
temperature above the boiling point of the solvent in a series
of U-tubes [7.16] or directly on a chromatographic column
[5.10]. All of these methods rely on the fact that the solvent
is much more volatile than the analyte. In the case of CO_2,
for instance, the separation is easily carried out at ambient
temperature, since the CO_2, after expansion to ambient
conditions is gaseous. For solvents with boiling points above
ambient temperature, it would be necessary to boil them off to
recover the analyte. This is a strong incentive to use low-
boiling solvents. This must presumably be born in mind when
using a volatile solvent (e.g. CO_2, which sublimes at $-78.5^{o}C$)
in conjunction with a not so volatile co-solvent (e.g.
methanol, which boils at $65^{o}C$). After expansion to ambient
pressure, the co-solvent may remain as a liquid. A co-solvent
which can be removed easily, or one which does not interfere
with subsequent analyses is therefore desirable.

74

10. Conclusions

10.1 Workplan to March, 1989

Work on the project was started September 1, 1987, even though funding started March 1, 1988. The first seven months were spent mainly on searching the literature and preparing this report.

The time from March 1, 1988 to the present has been spent assembling a small scale extraction apparatus using some of the parts (notably the pump) from the Milton-Roy X10 Supercritical Extraction System, which was supplied by MOE.

The gas chromatograph (a Varian model 3400) was recieved on July 22, 1988 and has been installed.

Some extractions have been performed on a sample of coal fly ash, as well as an NBS certified "Urban Dust" using carbon dioxide as the solvent. Initial results show that it is possible to perform several extractions and GC analyses per day using small (30-50 mg) samples of solid samples.

The time remaining to March 1, 1989 will be spent calibrating the GC for selected PAH compounds, and measuring the extraction efficiency of PAH with respect to pressure, temperature and time using pure supercritical solvents.

75

10.2 Projected costs

The costs are projected to be within the approved budget, which can be seen in Appendix I under "Detailed budget for option 3".
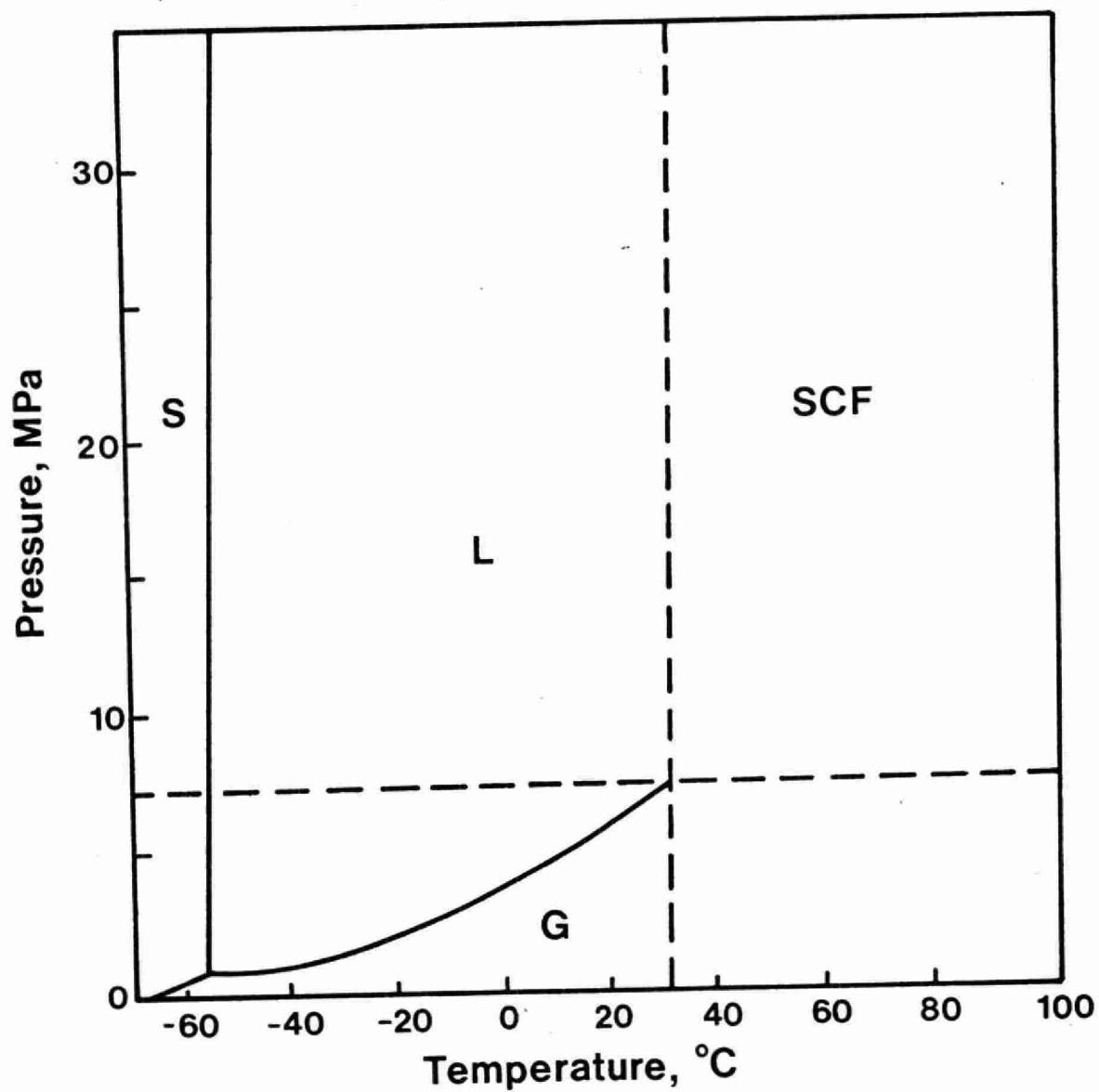
Figure 2.1 Pressure-temperature projection for carbon dioxide. The supercritical region is above and to the right of the dashed lines.

77
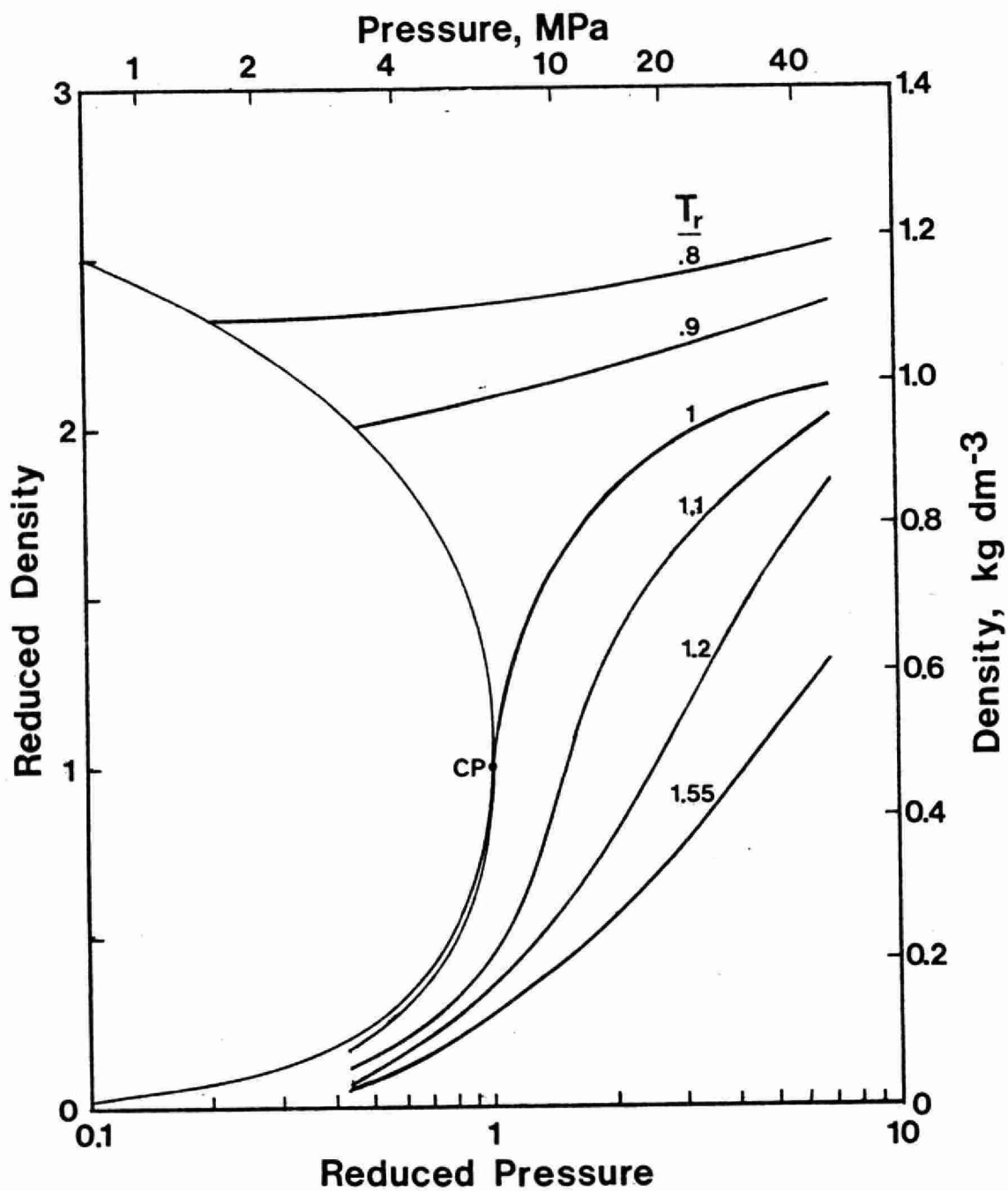
Figure 2.2. Density as a function of pressure for carbon dioxide in the critical region. The reduced temperature is shown for each curve.
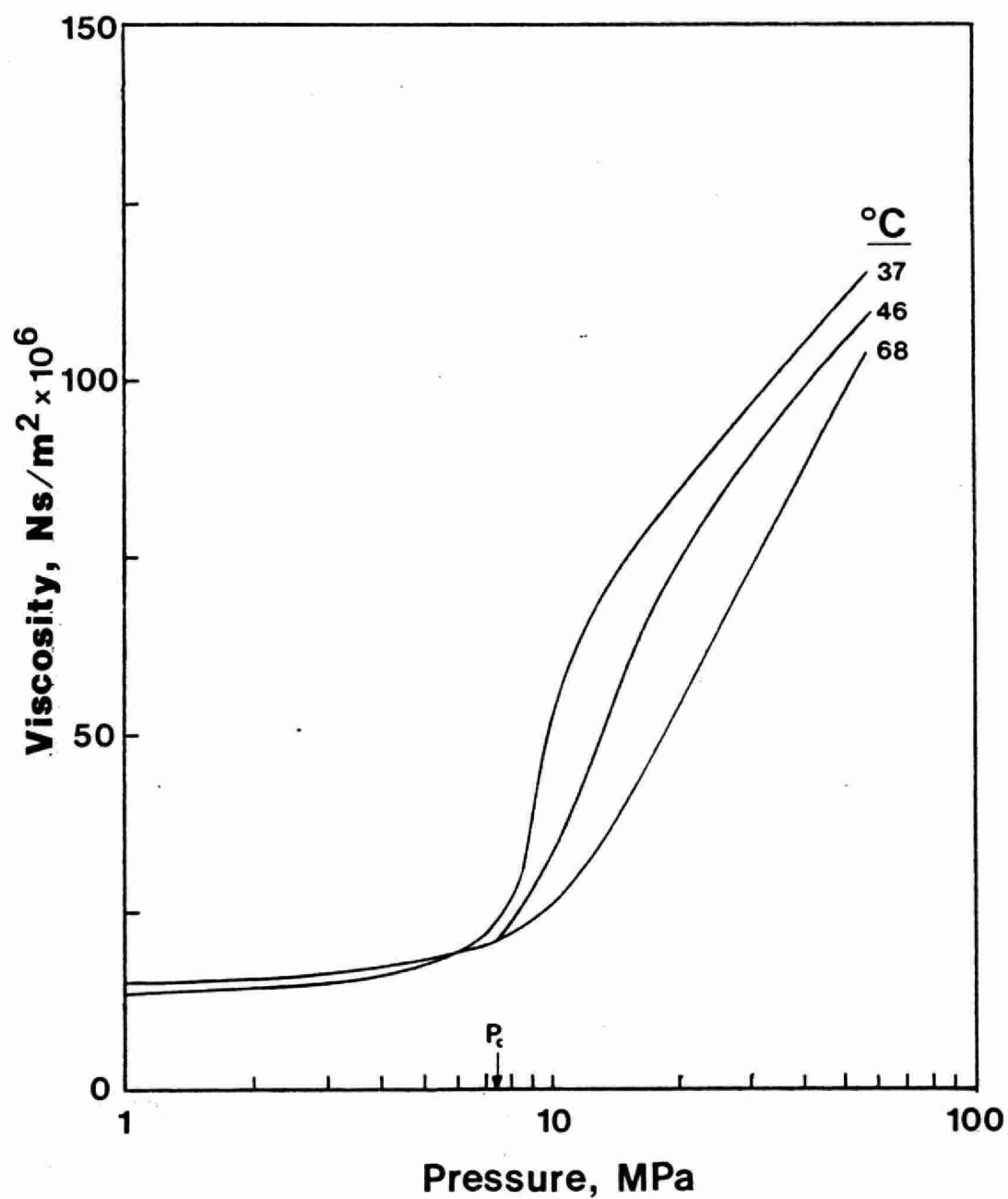
Figure 2.3. Viscosity of carbon dioxide as a function of pressure at various temperatures. The critical pressure of carbon dioxide is indicated on the axis.
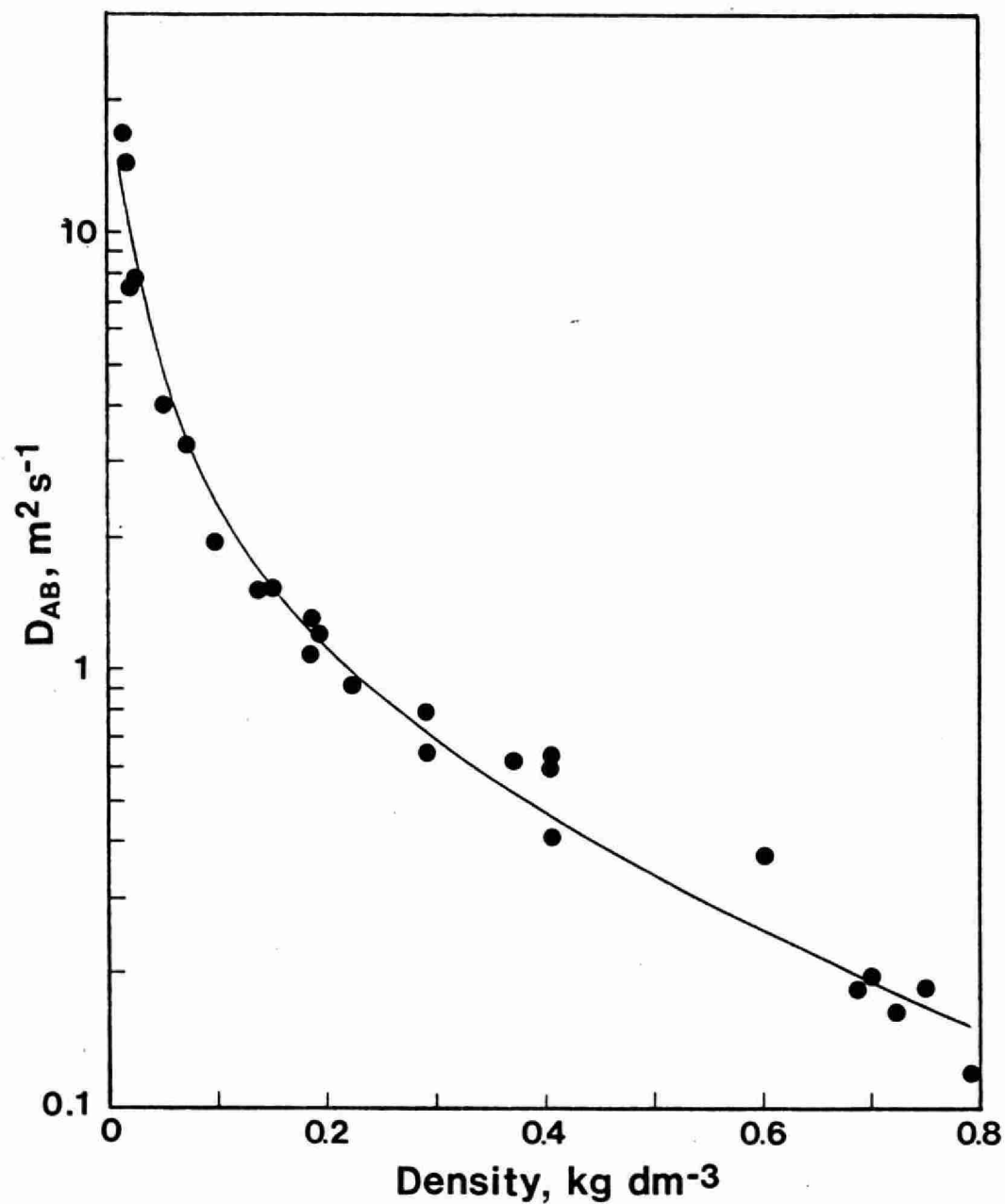
Figure 2.4 Self diffusion coefficient of carbon dioxide as a function of pressure.
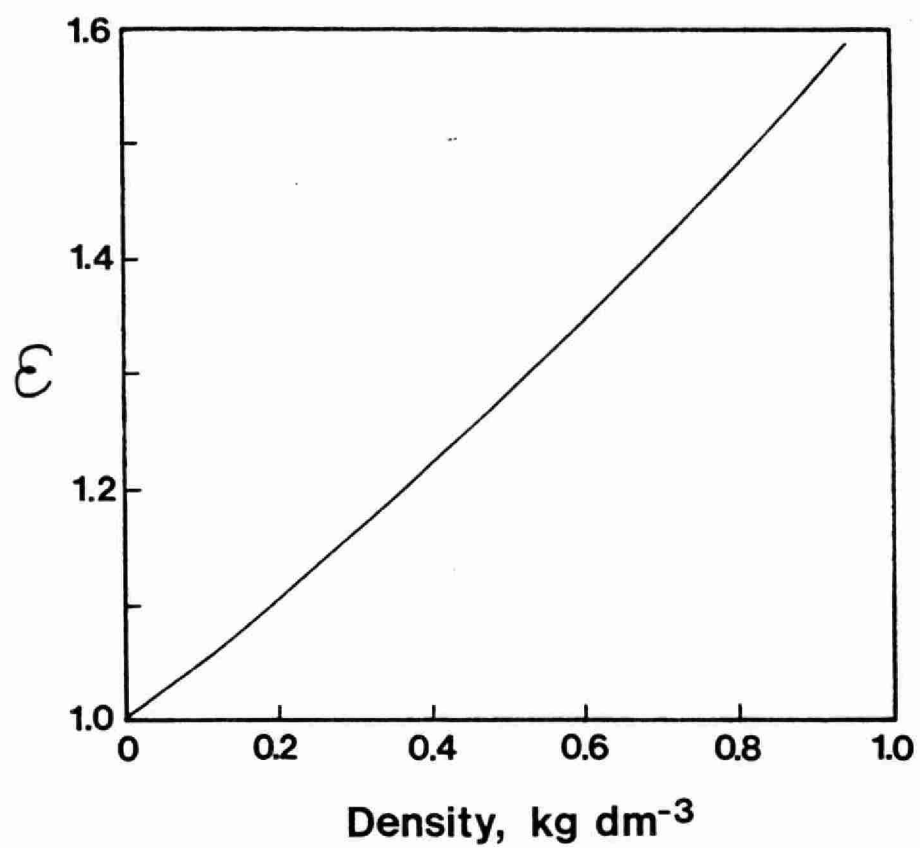
Figure 2.5 Dielectric constant of CO_2 as a function of density.
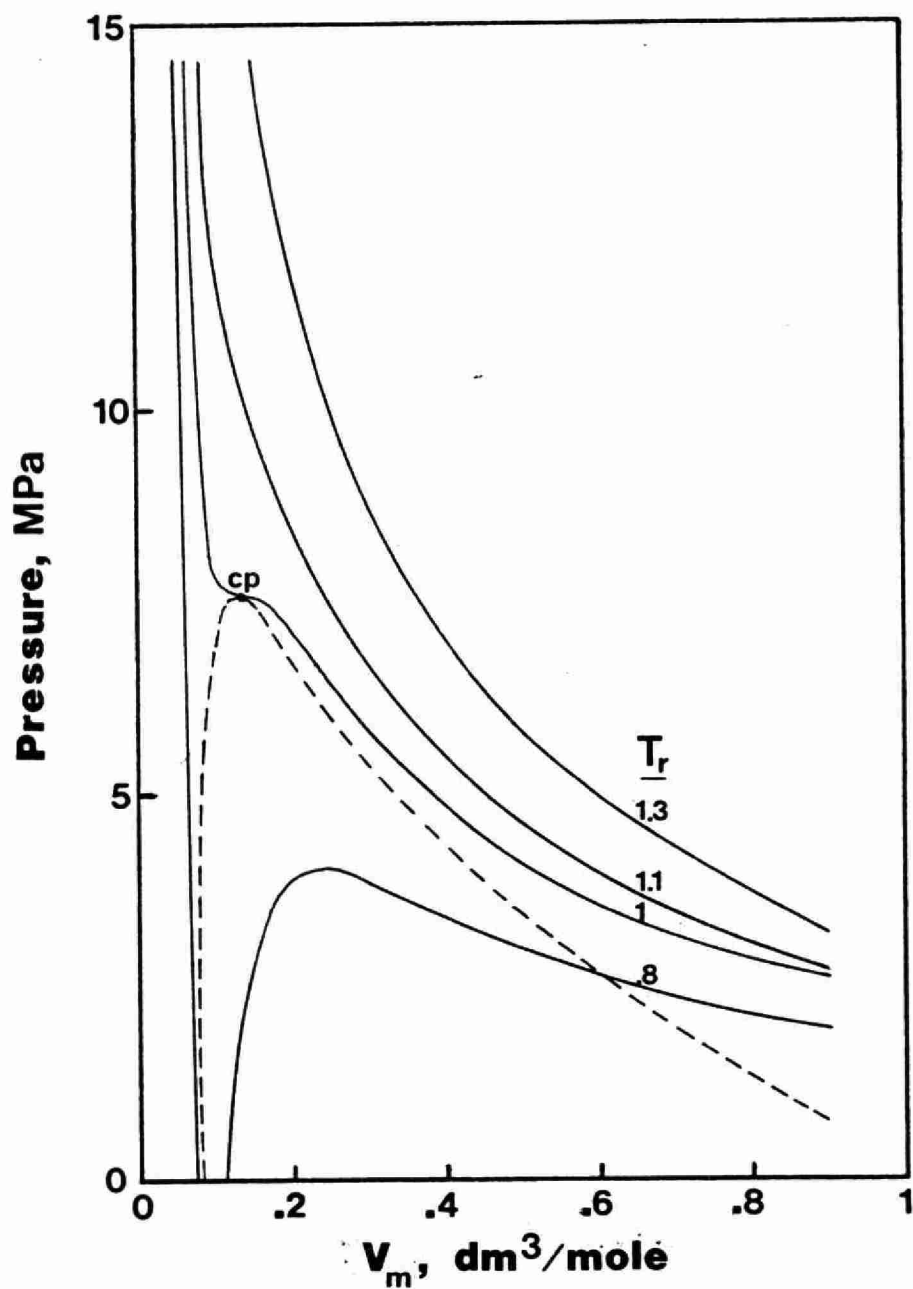
Figure 3.1. Pressure as a function of molar volume for carbon dioxide as calculated from the Van der Waals equation. The critical point is labelled 'cp'. The numbers on the graph indicate the reduced temperature. The two-phase region is below the dashed line.

82
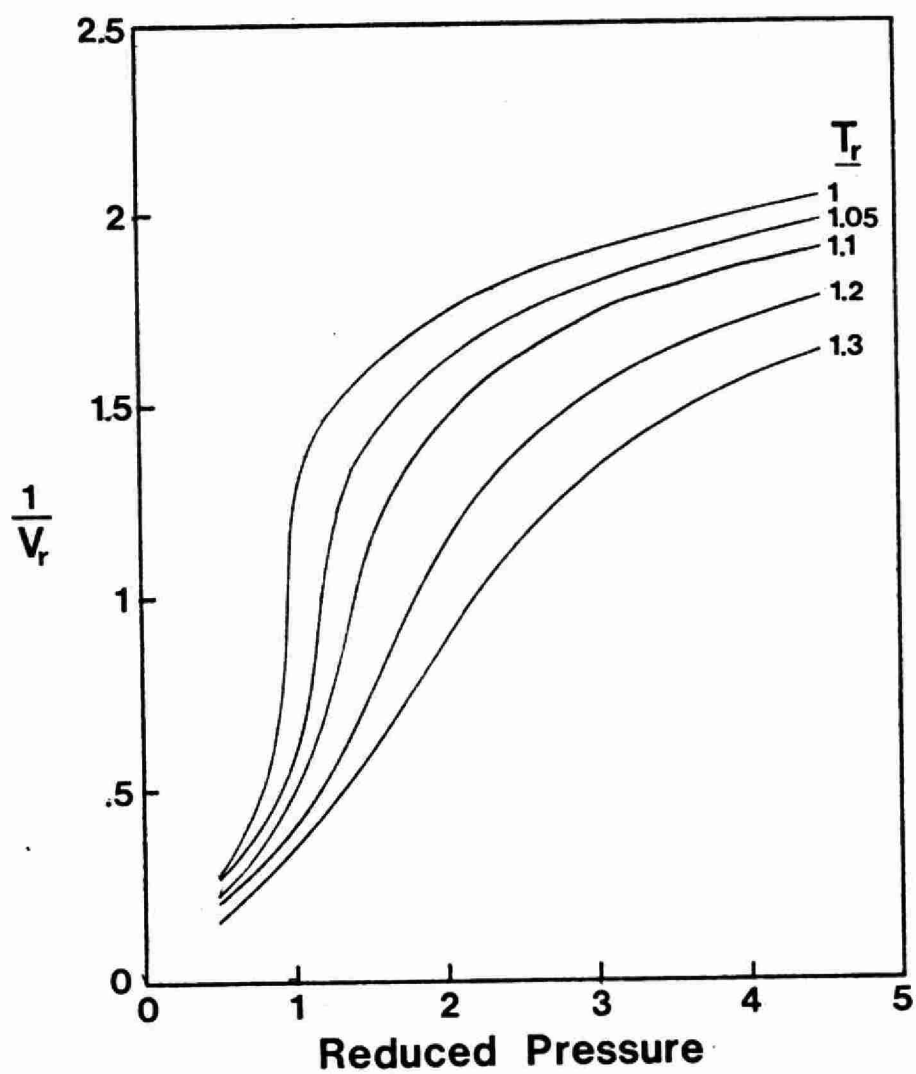
Figure 3.2. Universal plot of (1/molar volume) as a
function of pressure at various reduced temperatures.
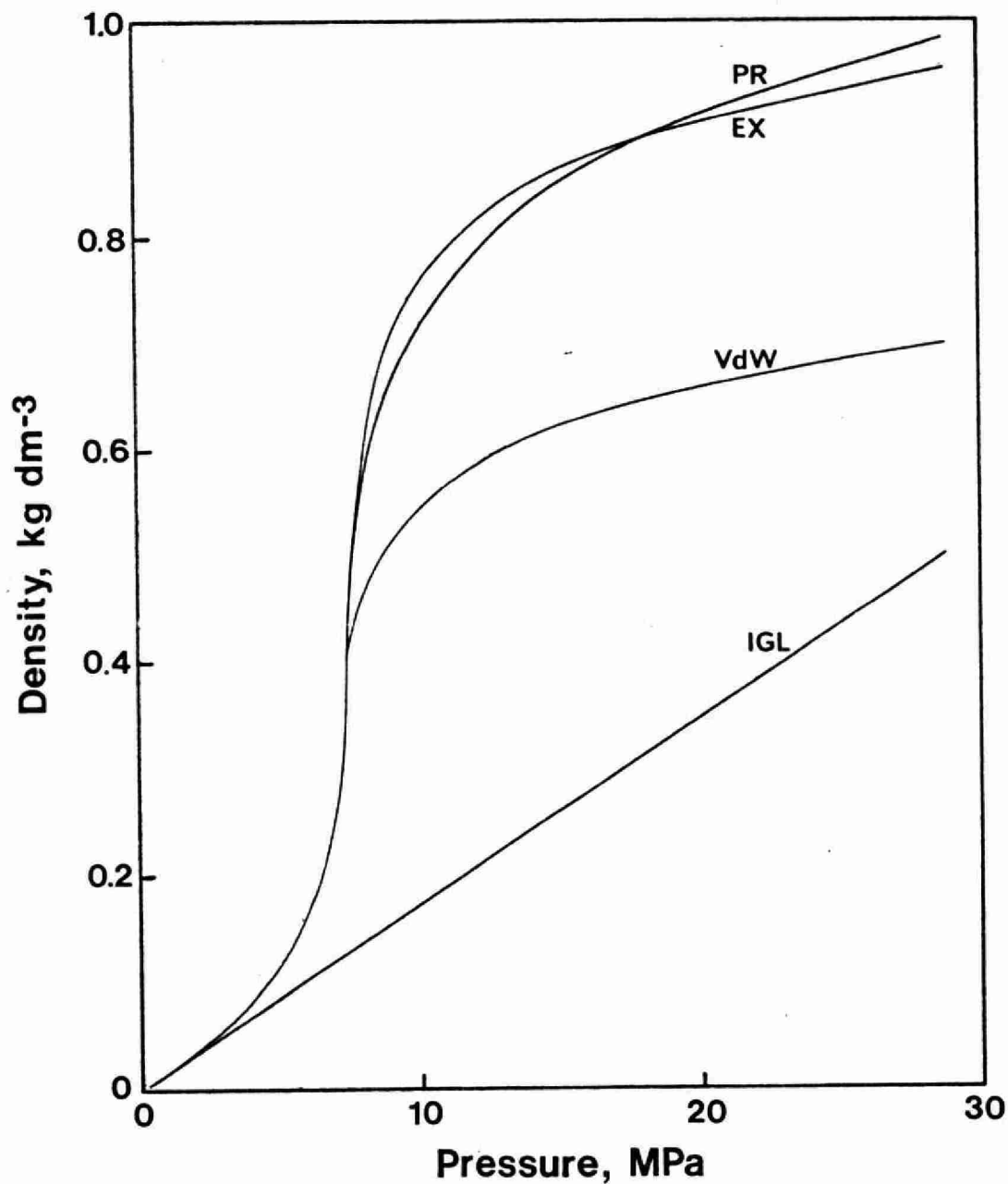
Figure 3.3. Density of carbon dioxide as a function of pressure at the critical temperature. The curves are found from:

        PR - Peng-Robinson equation of state
        EX - Experiment
        VdW - Van der Waals equation of state
        IGL - Ideal gas law
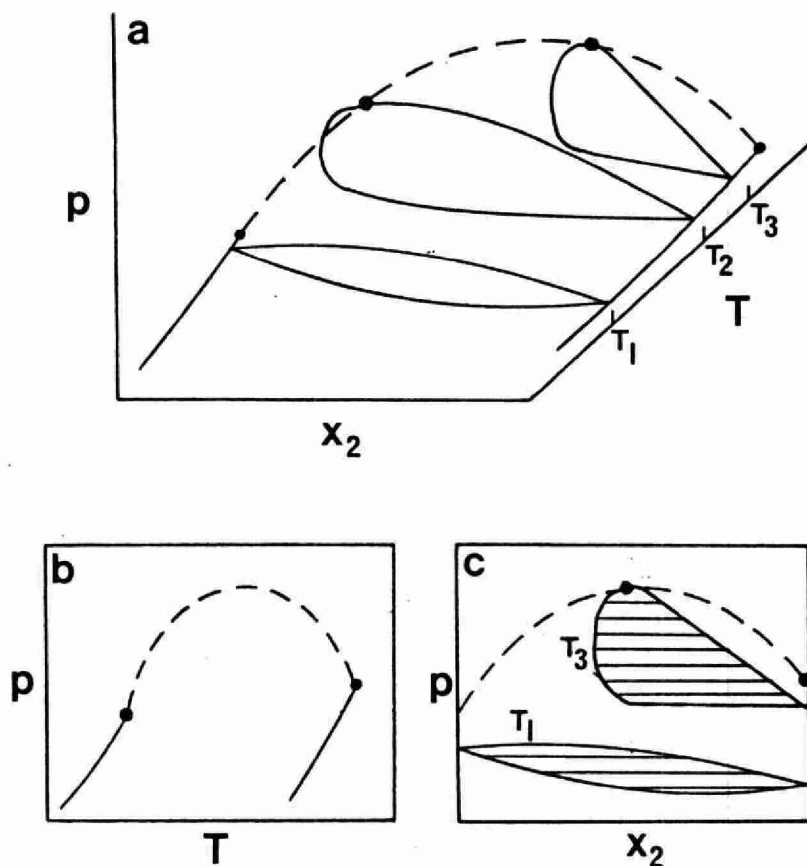
Figure 4.1 (a) A pTx diagram for a simple binary system. The critical curves for the two components and for the mixture are shown. Three constant temperature planes are also shown.

(b) A pT projection of the critical lines from figure 4.1a.

(c) A px diagram showing two of the constant temperature planes and the critical locus curve of figure 4.1a.
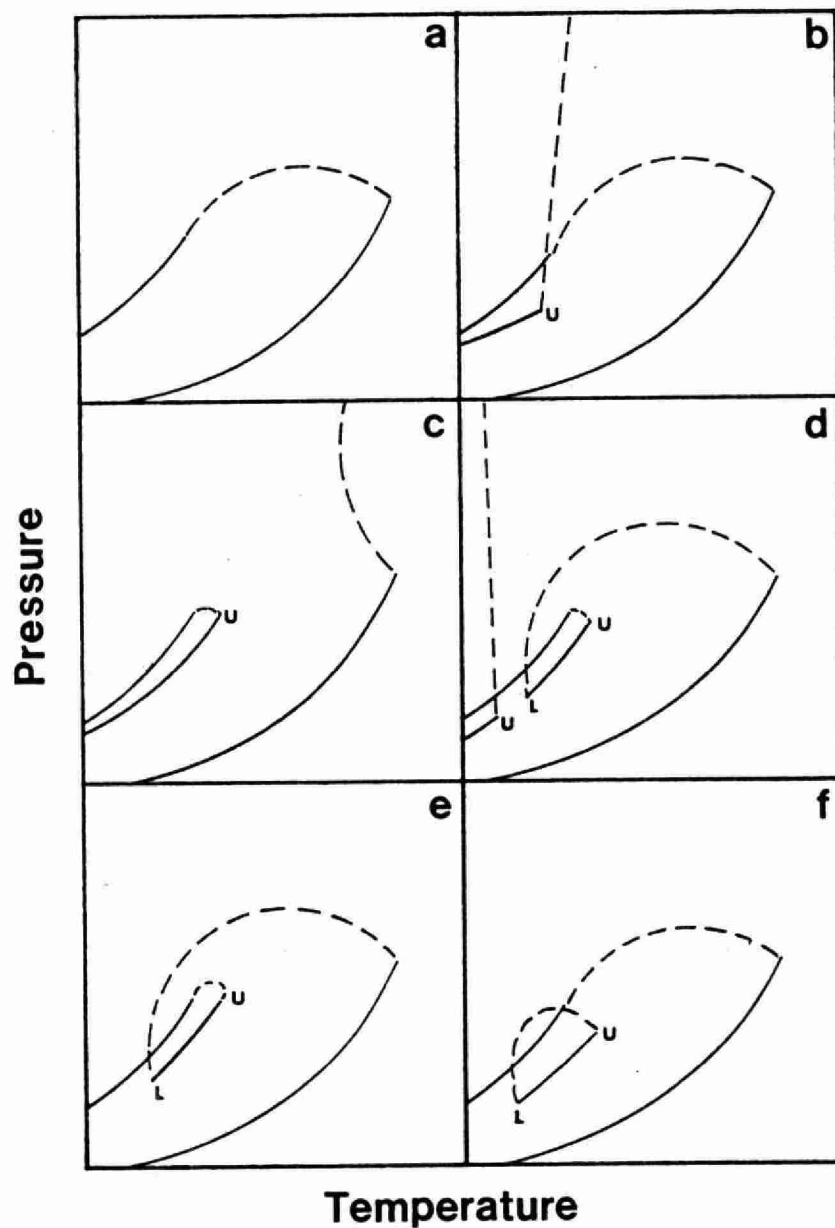
Figure 4.2. Pressure temperature projections of the six classifications of binary phase diagrams. U and L are the upper and lower critical endpoints, respectively. From reference 3.4.

86
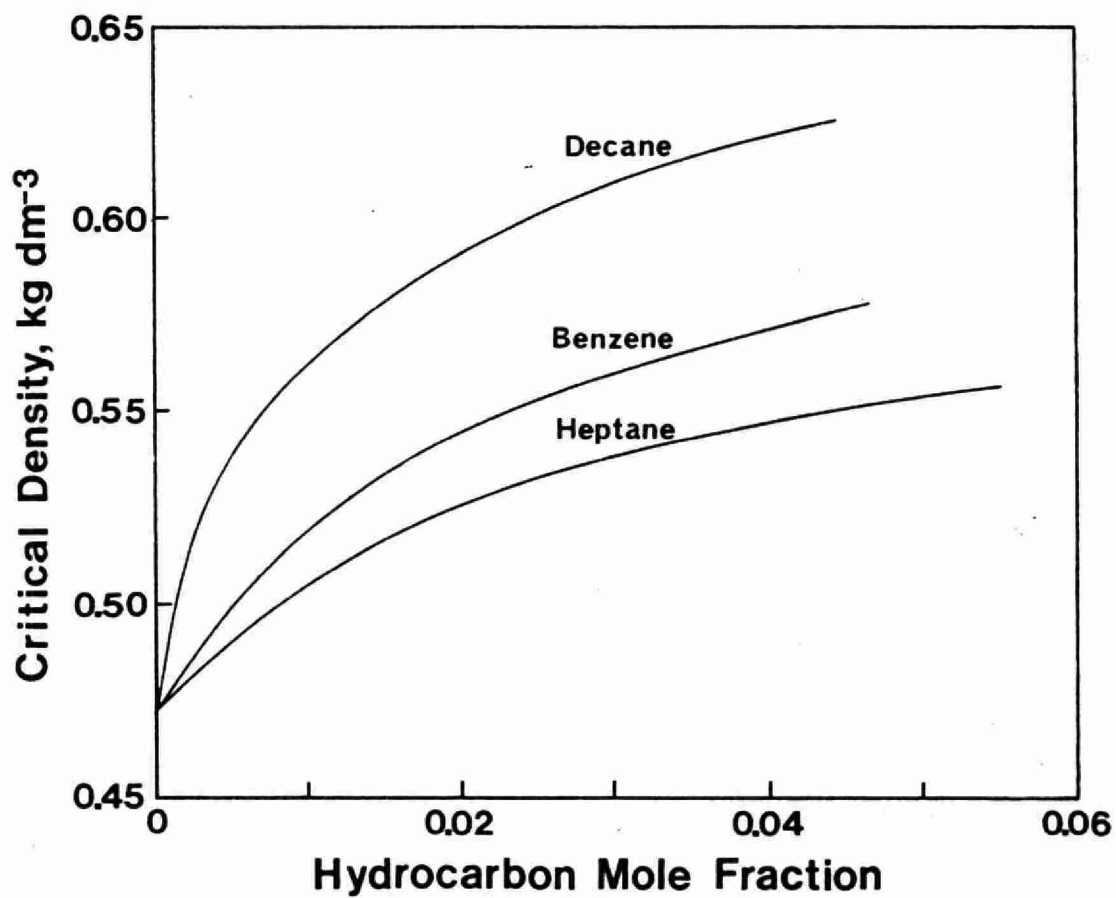
Figure 5.1. Critical density versus hydrocarbon mole
fraction for three carbon dioxide + hydrocarbon
binaries.

87
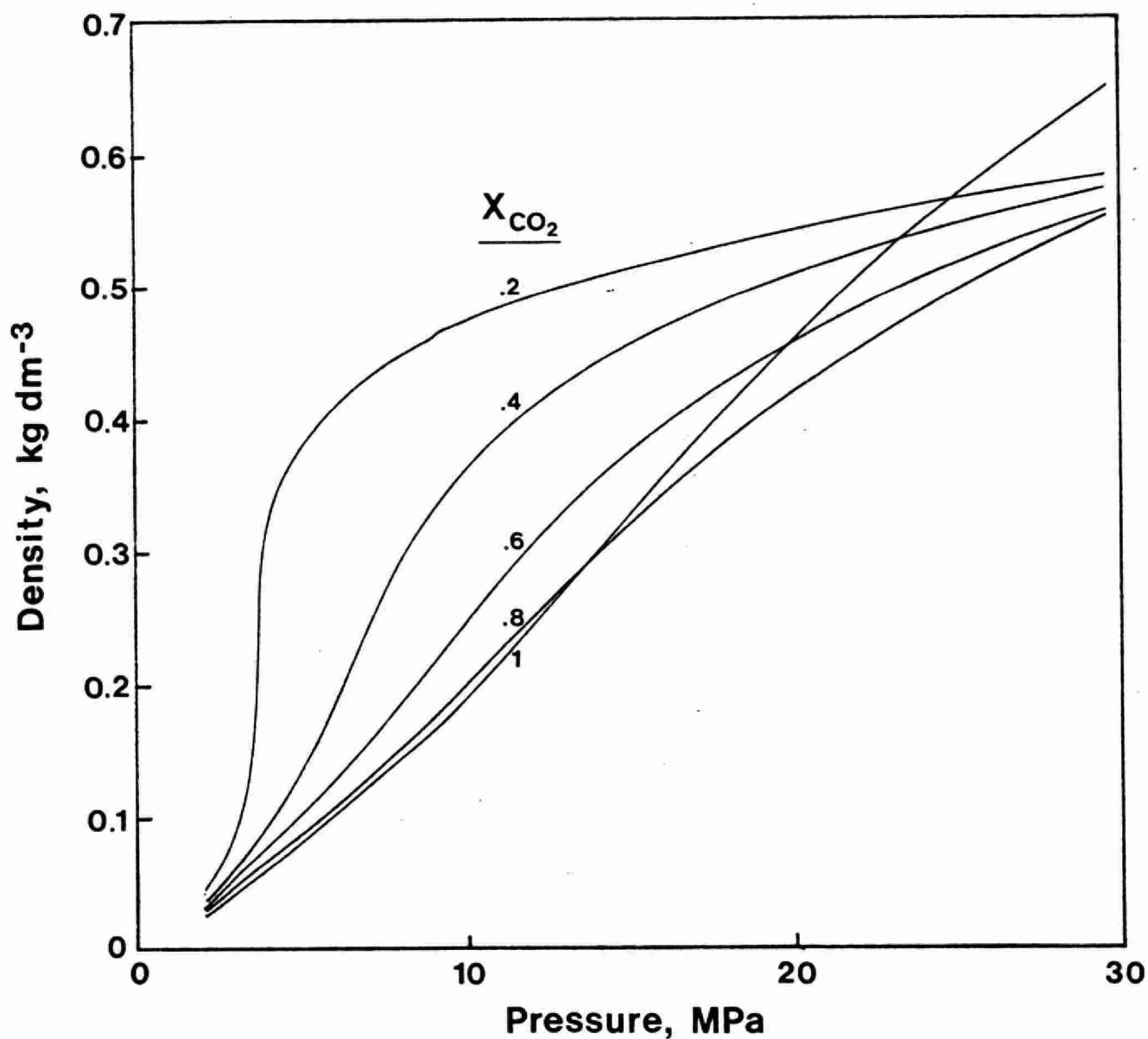
Figure 6.1. Density of the system carbon dioxide + n-butane at 90°C as a function of pressure calculated from the Peng-Robinson equation at various mole fractions of carbon dioxide.
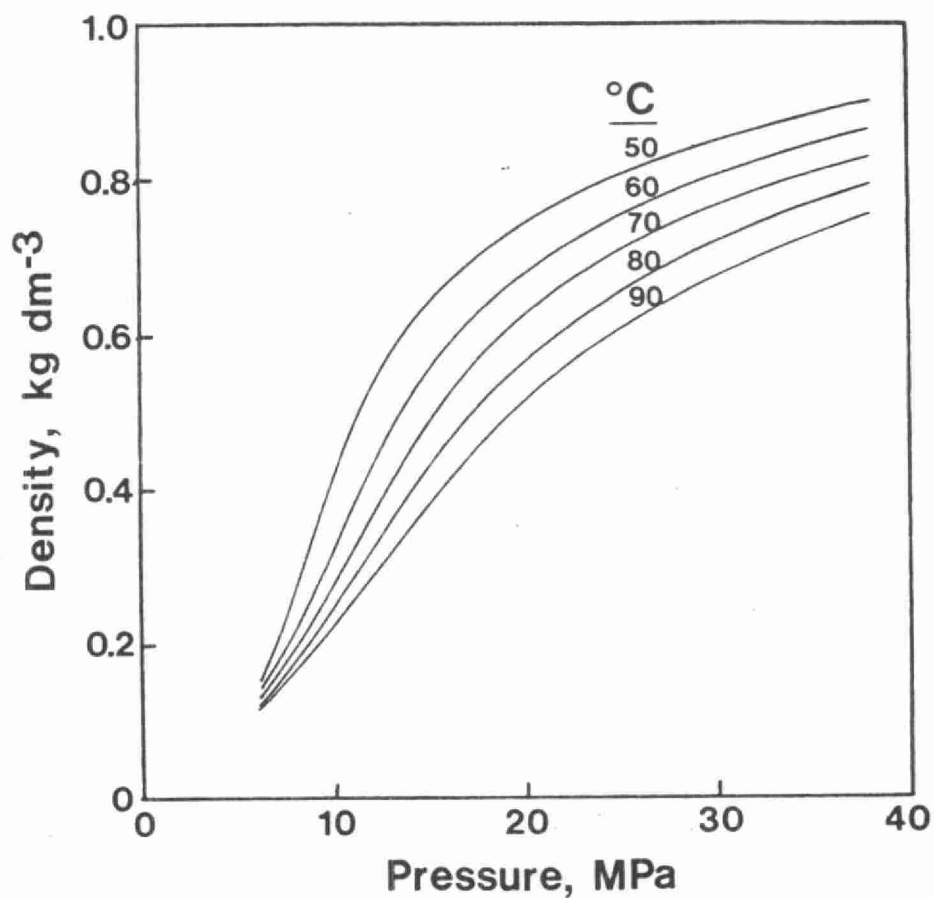
Figure 6.2 Density of the system carbon dioxide + 5%
n-butane as a function of pressure calculated from the
Peng-Robinson equation of state at various
temperatures.

Table 4.1. Some Example Binary System Classifications

Class I   carbon dioxide + n-butane

                 carbon dioxide + nitrous oxide

                 carbon dioxide + oxygen

                 carbon dioxide + ethane

                 methane + ethane

                 methane + nitrogen

                 benzene + methanol

                 benzene + cyclohexane

                 benzene + toluene

                 n-hexane + cis-decalin

                 argon + krypton

                 sulfur dioxide + chloromethane

                 hydrogen chloride + dimethyl ether

                 hydrogen chloride + ethane

Class II   carbon dioxide + n-heptane

                 carbon dioxide + n-octane

                 xenon + hydrogen chloride

                 n-pentane + nitrobenzene

Class III   carbon dioxide + tridecane

                 carbon dioxide + squalene

                 carbon dioxide + squalane

                 carbon dioxide + water

                 ethane + methanol

Table 4-1 continued

Class III ethane + water

      ethane + N,N-dimethylformamide

      ethane + nitromethane

      ethane + 2,5-hexanediol

      ethane + n-methylacetamide

      ammonia + argon

      ammonia + nitrogen

      ammonia + methane

      benzene + water

Class IV carbon dioxide + nitrobenzene

      carbon dioxide + 2-nitrophenol

      methane + 1-hexexe

Class V ethane + ethanol

      ethane + 1-propanol

      ethane + 1-butanol

      methane + n-hexane

Class VI water + 2-butanone

Table 6.1. Critical temperatures and pressures estimated by the method of Soulie and Rey.

FORMULA	NAME	T_c (°C)	P_c (MPa)
C_2H_6SO	Dimethyl sulfoxide	214.6	5.94
C_4H_8O	Tetrahydrofuran	245.8	3.98
C_5H_9NO	N-methyl-pyrollidinone	482.4	5.94
C_3H_3N	Acrylonitrile	268.2	4.63
C_3H_7NO	Dimethylformamide	392.0	6.23

Table 6.2. Critical temperatures, pressures, and densities of
solvents. The densities were calculated from the
Peng-Robinson equation of state.

FORMULA	NAME	T_c (^{o}C)	P_c (MPa)	ρ_c (kg dm^{-3})
CCl_4	Carbon Tetrachloride	283.2	4.56	0.495
$CHClF_2$	Chlorodifluoromethane	96.1	4.99	0.458
$CHCl_2F$	Dichlorofluoromethane	178.5	5.17	0.462
$CHCl_3$	Chloroform	262	5.53	0.484
CHF_3	Trifluoromethane	25.9	4.87	0.447
CH_3NO_2	Nitromethane	314.8	6.31	0.257
CH_4	Methane	-82.3	4.71	0.155
CH_4O	Methanol	239.4	8.02	0.196
CO_2	Carbon Dioxide	31.0	7.63	0.432
CS_2	Carbon Disulfide	276	7.65	0.416
C_2HCl_3	Trichloroethylene	271	5.02	0.475
$C_2H_2Cl_2$	cis-1,2-dichloroethylene	271	5.87	0.410
$C_2H_2Cl_2$	trans-1,2-dichloroethylene	243.3	5.51	0.406
C_2H_3N	Acetonitrile	247.7	4.83	0.149
$C_2H_4Cl_2$	1,1-dichloroethane	249.8	5.07	0.376
$C_2H_4F_2$	1,1-difluoroethane	113.5	4.50	0.301
C_2H_4O	Acetaldehyde	187.8	5.54	0.207
$C_2H_4O_2$	Acetic acid	321.6	5.79	0.229

Table 6.2 continued

FORMULA	NAME	T_c (^{o}C)	P_c (MPa)	ρ_c (kg dm^{-3})
C_2H_6	Ethane	32.2	4.89	0.188
C_2H_6O	Ethanol	243	6.38	0.223
C_2H_6O	Dimethyl ether	126.9	5.32	0.240
C_2H_6S	Dimethyl sulfide	228.9	5.53	0.268
C_2H_7N	Ethylamine	183.2	5.62	0.217
C_2H_7N	Dimethylamine	164.6	5.31	0.214
C_3H_6O	Acetone	235.6	4.75	0.212
$C_3H_6O_2$	Methyl acetate	233.7	4.69	0.268
$C_3H_6O_2$	Ethyl formate	235.5	4.71	0.289
C_3H_8	Propane	96.8	4.27	0.199
C_3H_8O	n-Propanol	263.7	5.10	0.233
C_3H_8O	Ethyl methyl ether	164.7	4.40	0.236
C_3H_9N	Trimethylamine	160.1	4.07	0.217
C_4H_4O	Furan	213.8	5.35	0.291
C_4H_8O	Methyl ethyl ketone	262.5	4.15	0.219
$C_4H_8O_2$	Ethyl acetate	250.2	3.84	0.253
$C_4H_8O_2$	Methyl propanoate	257.4	3.99	0.259
C_4H_{10}	n-Butane	152.3	3.75	0.200
C_4H_{10}	2-Methylpropane	135.0	3.70	0.206
$C_4H_{10}O$	tert-Butyl alcohol	235.0	4.96	0.283

Table 6.2 continued

FORMULA	NAME	T_c (°C)	P_c (MPa)	ρ_c (kg dm^{-3})
$C_4H_{10}O$	Diethyl ether	193.4	3.61	0.224
$C_4H_{11}N$	Diethyl amine	223.5	3.88	0.224
C_5H_5N	Pyridine	346.8	5.63	0.281
C_5H_{10}	Cyclopentane	238.6	4.52	0.242
$C_5H_{10}O$	Methyl n-propyl ketone	290.8	3.89	0.222
C_5H_{12}	n-Pentane	196.9	3.35	0.201
C_6H_5Cl	Chlorobenzene	359.2	4.52	0.315
C_6H_6	Benzene	289.4	4.96	0.270
C_6H_{12}	Cyclohexane	280.4	4.06	0.242
C_6H_{14}	Hexane	234.5	3.03	0.201
$C_6H_{15}N$	Triethylamine	260.1	3.04	0.226
C_7H_8	Toluene	320.4	4.23	0.257
C_7H_{16}	n-Heptane	267	2.73	0.198
C_8H_8	Styrene	374.4	3.99	0.251
C_8H_{10}	Ethylbenzene	345.6	3.78	0.254
C_8H_{10}	p-Xylene	344	3.55	0.239
C_8H_{18}	Octane	296.2	2.50	0.196
C_9H_{20}	Nonane	321.5	2.30	0.194
$C_{10}H_8$	Napthalene	476.6	4.11	0.275

Table 6.2 continued

FORMULA	NAME	T_c (°C)	P_c (MPa)	ρ_c (kg dm^{-3})
NH_3	Ammonia	132.4	11.46	0.188
H_2O	Water	374.2	22.12	0.241
SO_2	Sulfur dioxide	157.4	7.96	0.464
N_2	Nitrogen	-146.9	3.45	0.300
H_2S	Hydrogen Sulfide	100.4	9.16	0.327
Ar	Argon	-122.4	4.94	0.514
HCl	Hydrochloric acid	51.5	8.43	0.371
N_2O	Nitrous oxide	36.4	7.39	0.412
O_2	Oxygen	-118.5	5.05	0.409
SF_6	Sulfur hexafluoride	45.6	3.82	0.686
Xe	Xenon	16.6	6.00	1.065
	Air	-140.7	3.83	0.326

Table 6.2 continued

FORMULA	NAME	T_c ($^{\circ}C$)	P_c (MPa)	ρ_c (kg dm^{-3})
NH_3	Ammonia	132.4	11.46	0.188
H_2O	Water	374.2	22.12	0.241
SO_2	Sulfur dioxide	157.4	7.96	0.464
N_2	Nitrogen	-146.9	3.45	0.300
H_2S	Hydrogen Sulfide	100.4	9.16	0.327
Ar	Argon	-122.4	4.94	0.514
HCl	Hydrochloric acid	51.5	8.43	0.371
N_2O	Nitrous oxide	36.4	7.39	0.412
O_2	Oxygen	-118.5	5.05	0.409
SF_6	Sulfur hexafluoride	45.6	3.82	0.686
Xe	Xenon	16.6	6.00	1.065
	Air	-140.7	3.83	0.326

Table 7.1. Procedures for extraction of PAH from various
matrices.

Group	Group Type	Examples	Extraction Procedure
1	Soluble in the extraction solvent	Vegetable oils, fats, some biological materials, fuels	Dilution with solvent
2	Liquids, insoluble in the extraction solvent	Water, solutions of water-soluble salts	Distribution between matrix and extraction solvent
3	Not soluble in the extraction solvent	Vegetables, friuts	Homogenization, extraction with acetone
4	Not, or partly insoluble in the extraction solvent, but saponifiable with alkali	Food, biological material	Saponification with KOH, followed by extraction with solvent

Table 7.1 continued

Group	Group Type	Examples	Extraction Procedure
5	Heterogeneous materials containing inorganic material	Aerosols, dusts, sediments, dusts, sewage	Extraction with acetone, then with xylene if necessary; Saponification of residue, and extraction by cyclohexane
6	Graphite-like materials	Soot, graphite, coal, peat	Repeated extraction with boiling xylene

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PROPOSAL FOR INVESTIGATION AND DEVELOPMENT OF SUPERCRITICAL FLUID EXTRACTION OF TRACE ORGANICS FROM ENVIRONMENTAL MATRICES

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A. INTRODUCTION

1. The aim of this project is to develop reliable and rapid methods for extraction of trace organics from environmental matrices using supercritical fluids. Selective extraction e.g. of polycyclic aromatic hydrocarbons (PAHs) will also be aimed for.

2. The project will be the major part of the Ph.D. research of Mr. Robert C. Burk, M.Sc., in the Chemistry Department at Carleton University. As such, it is planned to be of a duration of three years starting September,1987. The budget for the project is made up in the form of a grant, allowing a greater degree of academic freedom while still achieving the goals set out in section A1.

3. In order that the project be acceptable as a Ph.D. thesis, the approach will be taken that fundamental and general information regarding supercritical fluids for extraction will be obtained, in addition to the aims set out above. Some of the projects of more general interest in which cooperation with this laboratory have been considered in the past are supercritical fluid extraction of selected organics from tar sands (Dr. B. Sparks, NRC, Ottawa) and selective extraction of carbohydrates from seeds (Dr. G. Fulcher, Agriculture Canada, Ottawa).

4. Activities in the first year will be modest, when there is considerable course work to be done by Mr. Burk.

5. The Advisors for Mr. Burk's research at Carleton University will be Dr. Peeter Kruus and Dr. Robert Wightman. They will not charge for their time if the project is done on a grant basis as part of a Ph.D. thesis.

6. The proposed schedule of research activities is presented below. Five options for funding are presented, differing mainly in the choice of analytical equipment.

B. PROPOSED SCHEDULE OF ACTIVITIES

1. Review of literature: 6 months

In this first phase, Mr. Burk will do a literature review of the current methods for extraction of organics from environmental matrices, as well as the background research on supercritical fluids and supercritical

extraction. At the start of this phase, he will visit the MOE laboratories to acquaint himself with their specific requirements and the equipment available there. At the end of this phase, a report will be written by Mr. Burk detailing the current methods, and how they may be improved by supercritical fluid extraction technology. Depending on the route chosen to analyze the products of the extractions, the analytical equipment should be purchased during this phase. After review of the report by MOE personnel, phase 2 will be initiated.

2. Assembling and modification of equipment: 6 months

It is understood that the principle extraction equipment (a Milton Roy Supercritical Extraction Laboratory Methods Development System) will supplied by MOE. Some time will undoubtedly be spent in modifying the system, and adapting it for use with the chosen solvents, analytical equipment, etc. A decision will have to be made regarding the detection method i.e. to integrate the detection method with the extraction, or to use "batch" detection. It is anticipated that the latter approach will be chosen.
The four options regarding the analyses are:

(i)   Purchase a dedicated gas chromatograph
(ii) Purchase a dedicated gas chromatograph with mass spectrometric detector
(iii) Do the analyses at the MOE laboratories
(iv) Contract out the analyses

Option (iii) would be difficult for Mr. Burk to accomodate, due to his other duties at Carleton University as a graduate student.
Option (iv) is undesirable since poor turnaround time could adversely affect progress on the project.
Options (i) or (ii) would appear to be the most reasonable. A gas chromatograph will almost certainly be required to analyze the complex extracts anticipated. A mass spectrometric detector, such as the Finnigan model 800 ion trap detector or the Hewlett Packard MSD would allow detection of difficult to separate compounds, and ensure accurate identifications.

3. Fundamental Studies: 12 months

In this phase, a combination of theoretical (thermodynamic analysis, application of solution theories) and experimental studies will be carried out to provide a framework for the potentials and limitations of supercritical fluid extraction. This stage is best carried out with standardized samples e.g. a sample of PAH on sand. The variables to be studied will be:

(i) Solvent. There are relatively few restrictions to the solvent, with many possibilities other than CO_2. The Milton Roy apparatus has, however, an upper temperature limit of

100°C, which must be adhered to, or taken into consideration when the modifications are made.

(ii) Cosolvent. Methanol is the usual choice for a cosolvent in supercritical fluid extraction. There are, however many other choices. The choice of a cosolvent is important if selective extraction is to be achieved.

(iii) Pressure and temperature. Although the most significant factor appears to density (controlled mainly by pressure), the temperature variation may prove to be significant. (see Wright et al, "Analytical Supercritical Fluid Extraction of Adsorbent Materials", Anal. Chem., 59,38-44, 1987)

(iv) Configuration of extraction vessel, contact time, and physical state of matrix to be extracted are all possible parameters.

Another report will be written by Mr. Burk at the end of this phase. After discussions with MOE personnel, a plan for the optimization of the extraction process for the specific interests of MOE will be developed.

4. Optimization of equipment: 9 months

This stage will be more closely correlated with the MOE. It should be noted that although the time alloted for this phase is only 9 months, the activity will be considerably greater than in the previous phases, since Mr. Burk will have finished his course requirements, and can devote full time to his research project. Some more realistic samples will be used e.g. industrial wastes or soot from diesel fuel, coal or wood.

5. Writing of final report: 3 months

The final report for the project will be Mr. Burk's Ph.D. thesis.

C. PERSONNEL AND EQUIPMENT

Appropriate resumes of the three Carleton researchers who will be involved in the project are enclosed. Mr. Burk has had some experience in the area of extraction and analysis of trace organics. He also has worked for some years as a researcher in an industrial environment, and thus has an appreciation of the necessity of maintaining the primary aim of the project in view throughout the investigations. Professor Kruus has had decades of experience in solution physical chemistry, and professor Wightman in organic chemistry. Both of the Carleton advisors have had experience in collaboration with government laboratories.

There is considerable experience in the Ottawa area that the project can draw on. Ms. J. Lockwood of Farrington and Lockwood Co. Ltd. has considerable experience in trace organic analysis, and has expressed a willingness to assist if the project is in the form of a Ph.D. thesis. There is

additional expertise at the National Research Council, Agriculture Canada, and Environment Canada.

Carleton University has a very capable Science Technology Centre, which can provide design, construction and modification of equipment in house.

The analytical equipment required for the project is not currently on hand at Carleton. This equipment will thus have to be purchased, or alternative arrangements for analyses must be made. The former option is clearly more attractive. The proposed budget includes provisions for a GC or a GC with an MS detector, as well as the supplies necessary to set up and run the equipment for the three year period.

If the analytical equipment is purchased, then in order to allow rapid progress in the supercritical extraction research, it is recommended that a student assistant be hired for the equivalent of five months to carry out the preparation of the samples after extraction and prior to analysis (i.e. sample cleanup).

D. BUDGET

This budget assumes the conditions mentioned in section A and the project schedule mentioned in B. There is thus no overhead for the university, workshop rates are low, and no fees will be charged for professional advice from Carleton University faculty members, or from outside sources. The total cost depends mainly on the choice of how the analyses are to be done. If a GC-MS system is purchased, the two choices are a Hewlett-Packard GC-MSD system and a Finnigan 800 series Ion Trap Detector with a Varian 3400 gas chromatograph. Copies of quotations for both systems are attached. The totals for the five possible budgets are presented below, and detailed on the following pages.

Option 1
Purchase a Hewlett-Packard GC-MSD system

Year 1...$149,823
Year 2...$ 21,500
Year 3...$ 25,500

Total...$196,823

Option 2
Purchase a Finnigan 800 Ion Trap and Varian 3400 GC
Year 1...$101,500
Year 2...$ 21,500
Year 3...$ 25,500

Total...$148,500

Option 3
Purchase a GC system
Year 1...$ 61,500
Year 2...$ 21,500
Year 3...$ 25,500

Total...$108,500

Option 4
Contract out the analyses
Year 1...$ 32,000
Year 2...$ 28,000
Year 3...$ 37,000

Total...$ 97,000

Option 5
R.C.Burk does the analyses at MOE laboratories
Year 1...$ 27,000
Year 2...$ 20,000
Year 3...$ 24,000

Total..$ 71,000

Detailed budget for option 1

Year 1
Hewlett-Packard MSD system............................$118,323
Materials and supplies................................$ 8,000
Literature searching and report preparation..........$ 2,000
Workshop charges......................................$ 5,000
Travel..$ 3,000
Analytical assistant..................................$ 1,500
Stipend for Mr. Burk..................................$ 12,000
(He will be working as a teaching assistant, and thus
will not require the full normal stipend. The travel
allowance assumes four trips to MOE labs and attendance
at one conference.)
Total...$149,823

Year 2
Materials and supplies................................$ 4,000
Report preparation....................................$ 1,000
Workshop charges......................................$ 1,000
Travel..$ 2,000
Analytical assistant..................................$ 1,500
Stipend for Mr. Burk..................................$ 12,000
Total...$ 21,500

Year 3
Materials and supplies................................$ 3,000
Report preparation....................................$ 1,000
Workshop charges......................................$ 1,000
Travel..$ 2,000
Analytical assistant..................................$ 2,500
Stipend for Mr. Burk..................................$ 16,000
(This assumes no teaching responsibilities.)
Total...$ 25,500

Grand total for option 1..............................$198,823

Detailed budget for option 2

Year 1
Finnigan 800 Ion trap with Varian 3400 GC............$ 70,000
Materials and supplies................................$ 8,000
Literature searching and report preparation..........$ 2,000
Workshop charges......................................$ 5,000
Travel..$ 3,000
Analytical assistant..................................$ 1,500
Stipend for Mr. Burk..................................$ 12,000
(He will be working as a teaching assistant, and thus
will not require the full normal stipend. The travel
allowance assumes four trips to MOE labs and attendance
at one conference.)
Total...$101,500

Year 2
Materials and supplies................................$ 4,000
Report preparation....................................$ 1,000
Workshop charges......................................$ 1,000
Travel..$ 2,000
Analytical assistant..................................$ 1,500
Stipend for Mr. Burk..................................$ 12,000
Total...$ 21,500

Year 3
Materials and supplies................................$ 3,000
Report preparation....................................$ 1,000
Workshop charges......................................$ 1,000
Travel..$ 2,000
Analytical assistant..................................$ 2,500
Stipend for Mr. Burk..................................$ 16,000
(This assumes no teaching responsibilities.)
Total...$ 25,500

Grand total for option 2.............................$148,500

Detailed budget for option 3

Year 1
```
Gas chromatograph.........................................$ 30,000
Materials and supplies....................................$  8,000
Literature searching and report preparation..............$  2,000
Workshop charges..........................................$  5,000
Travel....................................................$  3,000
Analytical assistant......................................$  1,500
Stipend for Mr. Burk......................................$ 12,000
```
(He will be working as a teaching assistant, and thus
will not require the full normal stipend. The travel
allowance assumes four trips to MOE labs and attendance
at one conference.)
```
Total.....................................................$ 61,500
```

Year 2
```
Materials and supplies....................................$  4,000
Report preparation........................................$  1,000
Workshop charges..........................................$  1,000
Travel....................................................$  2,000
Analytical assistant......................................$  1,500
Stipend for Mr. Burk......................................$ 12,000
Total.....................................................$ 21,500
```

Year 3
```
Materials and supplies....................................$  3,000
Report preparation........................................$  1,000
Workshop charges..........................................$  1,000
Travel....................................................$  2,000
Analytical assistant......................................$  2,500
Stipend for Mr. Burk......................................$ 16,000
```
(This assumes no teaching responsibilities.)
```
Total.....................................................$ 25,500

Grand total for option 3..................................$108,500
```

Detailed budget for option 4

Year 1
Materials and supplies...............................$ 5,000
Literature searching and report preparation.........$ 2,000
Workshop charges....................................$ 5,000
Travel..$ 3,000
Outside analytical charges..........................$ 5,000
Stipend for Mr. Burk................................$ 12,000
(He will be working as a teaching assistant, and thus
will not require the full normal stipend. The travel
allowance assumes six trips to MOE labs and attendance
at one conference.)
Total...$ 32,000

Year 2
Materials and supplies...............................$ 2,000
Report preparation..................................$ 1,000
Workshop charges....................................$ 1,000
Travel..$ 2,000
Outside analytical charges..........................$ 10,000
Stipend for Mr. Burk................................$ 12,000
Total...$ 28,000

Year 3
Materials and supplies...............................$ 2,000
Report preparation..................................$ 1,000
Workshop charges....................................$ 1,000
Travel..$ 2,000
Outside analytical charges..........................$ 15,000
Stipend for Mr. Burk................................$ 16,000
(This assumes no teaching responsibilities.)
Total...$ 37,000

Grand total for option 4............................$ 97,000

NOTE: The analytical requirements were estimated to be
300 samples @ $100.

Detailed budget for option 5

Year 1
Materials and supplies...............................$ 5,000
Literature searching and report preparation.........$ 2,000
Workshop charges....................................$ 5,000
Travel..$ 3,000
Stipend for Mr. Burk................................$ 12,000
(He will be working as a teaching assistant, and thus
will not require the full normal stipend. The travel
allowance assumes four trips to MOE labs and attendance
at one conference.)
Total...$ 27,000

Year 2
Materials and supplies..............................$ 2,000
Report preparation..................................$ 1,000
Workshop charges....................................$ 1,000
Travel..$ 4,000
Stipend for Mr. Burk................................$ 12,000
Total...$ 20,000

Year 3
Materials and supplies..............................$ 2,000
Report preparation..................................$ 1,000
Workshop charges....................................$ 1,000
Travel..$ 4,000
Stipend for Mr. Burk................................$ 16,000
(This assumes no teaching responsibilities.)
Total...$ 24,000

Grand total for option 5............................$ 71,000

NOTE: The budget for this option assumes MOE will assume all
costs for analytical supplies.

Appendix II

Solutions of the Van der Waals and Peng-Robinson equations of state for a pure fluid

The Van der Waals' equation of state is expressed as

$$p = RT/(V_m - b) - a/V_m^2 \qquad \text{(II-1)}$$

thus,

$$pV_m^3 + (-pb - RT)V_m^2 + aV_m - ab = 0 \qquad \text{(II-2)}$$

Equation II-2 is a polynomial of the form

$$c_1 V_m^3 + c_2 V_m^2 + c_3 V_m + c_4 = 0 \qquad \text{(II-3)}$$

with constants

$$c_1 = p \qquad \text{(II-4)}$$

$$c_2 = -pb - RT \qquad \text{(II-5)}$$

$$c_3 = a \qquad \text{(II-6)}$$

$$c_4 = -ab \qquad \text{(II-7)}$$

which can be solved numerically for the roots. Above the critical temperature, there will be only one real root, corresponding to the molar volume of the gas. Below the critical point, there will be two real roots, corresponding to the molar volumes of the gas and the liquid phases.

The numerical routine used to solve for the roots of the polynomial was the Fortran version of the NAG (Numerical Algorithms Group) routine CO2AEF.

The values for a and b can be found from the critical pressure and temperature by rearranging equations 3.1.4 and 3.1.5 to give

$$a = 27R^2 T_c^2 / 64 p_c \qquad \text{(II-8)}$$

118

$$b = RT_c/8p_c \qquad \text{(II-9)}$$

Equation II-1 in reduced form is

$$p_r = 8T_r/(3V_r - 1) - 3/V_r^2 \qquad \text{(II-10)}$$

which can be solved for the reduced volume using the
polynomial constants

$$c_1 = 3p_r \qquad \text{(II-11)}$$

$$c_2 = -p_r - 8T_r \qquad \text{(II-12)}$$

$$c_3 = 9 \qquad \text{(II-13)}$$

$$c_4 = -3 \qquad \text{(II-14)}$$

The molar volume can then be found from

$$V_m = V_r V_c \qquad \text{(II-15)}$$

where $V_c = 3b$.

The Peng-Robinson equation can be solved in a similar
manner, except that the polynomial constants are

$$c_1 = p \qquad \text{(II-16)}$$

$$c_2 = pb - RT \qquad \text{(II-17)}$$

$$c_3 = -3pb^2 - 2RTb + a \qquad \text{(II-18)}$$

$$c_4 = pb^3 + RTb^2 - ab \qquad \text{(II-19)}$$

The molar volume can then be found from equation II-15, with
$V_c = 3.946b$.

Solving the Peng-Robinson equation in reduced form in
order to generate universal pressure-volume curves is not
possible, since the a term is temperature as well as species
dependent.

APPENDIX III. Computer Program for Calculating the Density
of a Two-Component Supercritical Fluid

```
 1.000          IMPLICIT REAL (A-Z)
 2.000          R=83.1439
 3.000          PC1=73.8
 4.000          TC1=304.2
 5.000          W1=0.225
 6.000          MW1=44.0
 7.000          PC2=38.0
 8.000          TC2=425.2
 9.000          W2=0.193
10.000          MW2=58.13
11.000          DELIJ=0.13
12.000          PRINT*,'ENTER X1:'
13.000          READ*,X1
14.000          X2=1-X1
15.000          AVGMW=X1*MW1+X2*MW2
16.000          TLOW=323.15
17.000          THIGH=363.15
18.000          TINC=10.
19.000          PRINT*,'PC1 = ',PC1,'   TC1 = ',TC1,'   W1 = ',W1
20.000          PRINT*,'PC2 = ',PC2,'   TC2 = ',TC2,'   W2 = ',W2
21.000          PRINT*,'DELIJ = ',DELIJ
22.000          PRINT*,'X1 = ',X1
23.000          ATC1=0.45724*R*R*TC1*TC1/PC1
24.000          ATC2=0.45724*R*R*TC2*TC2/PC2
25.000          K1=0.37464+1.54226*W1-0.26992*W1*W1
26.000          K2=0.37464+1.54226*W2-0.26992*W2*W2
27.000          BT1=0.0778*R*TC1/PC1
28.000          BT2=0.0778*R*TC2/PC2
29.000          B=X1*BT1+X2*BT2
30.000          DO 10 T=TLOW,THIGH,TINC
31.000          PRINT*,'T = ',T
32.000          PRINT*,''
33.000          AL1=(1+K1*(1-(T/TC1)**0.5))**2
34.000          AL2=(1+K2*(1-(T/TC2)**0.5))**2
35.000          AT1=ATC1*AL1
36.000          AT2=ATC2*AL2
37.000          A12=(AT1*AT2)**0.5*(1-DELIJ)
38.000          A=X1*X1*AT1+2*X1*X2*A12+X2*X2*AT2
39.000          DO 5 D1=0.1,1,.1
40.000          V=AVGMW/D1
41.000          D=D1
42.000          P=(R*T)/(V-B)-A/(V*(V+B)+B*(V-B))
43.000          IF(P.GT.400.OR.P.LE.0.0) GO TO 5
44.000          PRINT*,P,D
45.000     5    CONTINUE
46.000          PRINT*,''
47.000          PRINT*,''
48.000    10    CONTINUE
49.000          END
```

Appendix IV. Glossary of terms

Symbol	Meaning	Page	Equation
A	Helmholtz energy	18	3.3.9
A_{comp}	Helmholtz energy of compression	19	3.3.8
A_{mix}	Helmholtz energy of mixing	18	3.3.7
A^+	Helmholtz energy of perfect gases	18	3.3.9
a	Equation of state constant	11	3.1.3
a	Chrastil equation constant	31	3.4.29
B	Dielectric virial coefficient	9	2.4.2
b	Equation of state constant	10	3.1.3
b	Chrastil equation constant	31	3.4.29
C	Dielectric virial coefficient	9	2.4.2
C	Number of components (Gibbs equation)	33	4.1.1
c	Solute concentration in g L^{-1}	30	3.4.26
D_{AB}	Self diffusion coefficient	8	
E	Enhancement factor	22	3.4.2
F	Number of independent variables (Gibbs equation)	33	4.1.1
f_2^c	Pure solid solute fugacity	28	3.4.17
f_2^F	Fluid phase solute fugacity	22	3.4.3
f_2^{oL}	Pure liquid solute fugacity at pressure p_o	28	3.4.14
f_2^{os}	Pure solid solute fugacity at pressure p_o	28	3.4.17

Appendix IV continued

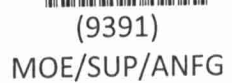| Symbol	Meaning	Page	Equation
f_2^s	Solid phase solute fugacity	22	3.4.3
G_m	Molar Gibbs energy	17	3.3.5
ΔH	Enthalpy of reaction	30	3.4.25
$\Delta H_{fus,2}$	Enthalpy of fusion of solute	29	3.4.19
ΔH_{solv}	Enthalpy of solvation	30	3.4.23
ΔH_{vap}	Enthalpy of vaporization	3	3.4.24
i	Component number	17	3.3.1
j	Component number	17	3.3.1
K	Equilibrium constant	29	3.4.21
K	Critical endpoint	35	
k	Boltzmann constant	9	2.4.1
k	Constant in Chrastil equation	29	3.4.20
k_{ij}	Binary interaction coefficient	17	3.3.3
LCST	Lower critical solution temperature	36	
l_{ij}	Binary interaction coefficient	17	3.3.3
MW	Molecular weight	15	3.2.1
N	Number of molecules	9	2.4.1
P	Number of phases (Gibbs equation)	33	4.1.1
PAH	Polycyclic aromatic hydrocarbon(s)		
p	Pressure	5	2.1.2
p_A	Attraction pressure	10	3.1.2
p_c	Critical pressure	5	2.1.2

122

Appendix IV continued

Symbol	Meaning	Page	Equation
p_o	Reference pressure	28	3.4.14
p_R	Repulsion pressure	10	3.1.2
p_r	Reduced pressure	5	2.1.2
p_2^{sat}	Solute saturation vapor pressure	21	3.4.1
q	Constant	30	3.4.25
q_s	Constant	30	3.4.23
q_v	Constant	30	3.4.24
R	Gas constant	10	3.1.1
SCF	Supercritical fluid		
SFC	Supercritical fluid chromatography		
SFE	Supercritical fluid extraction		
ΔS_{mix}	Entropy of mixing	18	
T	Temperature	5	2.1.1
T_c	Critical temperature	5	2.1.1
T_r	Reduced temperature	5	2.1.1
$T_{m,2}$	Solute melting temperature	29	3.4.19
UCST	Upper critical solution temperature	35	
V	Volume	18	
$V_{c,m}$	Critical molar volume	11	3.1.6
V^F	Fluid phase molar volume	26	3.4.11
V_m	Molar volume	9	2.4.1

Appendix IV continued

Symbol	Meaning	Page	Equation
V_r	Reduced volume	12	3.1.8
V_2	Molar volume of solute	22	3.4.4
$\bar{v}_2$	Partial molar volume of solute	26	3.4.14
$V_{2,m}^c$	Molar volume of condensed solute	28	3.4.17
$\bar{v}_{2,m}$	Partial molar volume of solute at infinite dilution	28	3.4.15
V_2^s	Molar volume of pure solid solute	22	3.4.5
v^+	Total volume of two separate perfect gases	18	3.3.9
x_i	Mole fraction of component i	17	3.3.1
y_2	Solute mole fraction	22	3.4.2
y_2^o	Ideal solute mole fraction	21	3.4.1
z	Compressibility factor	24	3.4.10
z_c	Critical compressibility factor	11	3.1.7
$\propto$	Constant in Peng–Robinson equation	13	3.1.13
$\propto_o$	Mean molecular polarizability	9	2.4.1
γ_2	Solute activity coefficient	28	3.4.14
γ_2^∞	Solute activity coefficient at infinite dilution	28	3.4.18
κ	Constant in Peng–Robinson equation	13	3.1.15
ϵ	Dielectric constant	9	2.4.1

124

Appendix IV continued

Symbol	Meaning	Page	Equation
μ_o	Dipole moment	9	2.4.1
ν	Absorption maximum wavelength in test solvent	32	3.4.30
ν_o	Absorption maximum wavelength in reference solvent	32	3.4.30
π	Pi (3.1415927)	9	2.4.1
π^*	Solvent polarity parameter	32	3.4.30
ρ	Density	15	3.2.1
φ_2^F	Fluid phase solute fugacity coefficient	23	3.4.8
φ_2^{sat}	Solute fugacity coefficient at saturation vapor pressure	23	3.4.6
ω	Acentric factor	13	3.1.15

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